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PILOT-SCALE EVALUATION OF LIMB TECHNOLOGY

Final Report

by

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16. ABSTRACT

The report gives results of pilot-scale studies of sulfur capture in the EPA's Limestone Injection Multistage Burner (LIMB) process and the effect of LIMB on particulate properties and electrostatic precipitator (ESP) performance. The sulfur capture studies showed that hydrated lime was generally superior to limestone as a sorbent for in-furnace sulfur removal. For both sorbents, downstream injection was found to be preferable over near-flame injection. With hydrated lime, the optimum injection temperature was found to be about 1200 C, where utilizations as high as 30% were achieved. The injection of either sorbent resulted in a large increase in the electrical resistivity of the ash, which could severely impact ESP performance. Laboratory and pilot-scale studies showed that the resistivity increase could be offset by flue gas conditioning using sulfur trioxide (SO3) or water vapor. With limestone injection, acceptable resistivity levels were restored by the injection of 30 ppm of SO3.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Sulfur	Pollution Control	13B	
Coal	Particles	Stationary Sources	21D	14G
Natural Gas	Sulfur Trioxide	Limestone Injection		
Combustion	Electrostatic Precipitators	Multistage Burners	21B	
Limestone		Particulate	08D	13I
Calcium Oxides	Electrical Resistivity		07B	20C

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PREFACE

The research described in this report was initiated in July 1982. The original scope of work was limited to the effects of Limestone Injection Multistage Burner (LIMB) technology on the characteristics of fly ash and the performance of electrostatic precipitators (ESPs). These were aspects of LIMB technology that had not been addressed prior to this study. During the particulate measurements with LIMB, data on sulfur capture were also obtained. In some cases, these data were not in agreement with sulfur capture data obtained by other investigators. This prompted an expansion of the project scope to include studies of sulfur capture as a function of sorbent type and process conditions. Thus, this report contains data from two areas of research: (1) Studies of sulfur capture in the LIMB process, and (2) Studies of particulate properties and ESP performance with LIMB.

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

This report presents the results of research performed in two separate areas of Limestone Injection Multistage Burner (LIMB) technology: (1) Sulfur capture in the LIMB process, and (2) Particulate properties and ESP performance with LIMB. In the first area, the research program included studies of sulfur capture as a function of sorbent type, injection location, furnace load, burner stoichiometry, and time-temperature profile. The sorbent utilization as a function of particle size was also investigated using size fractionated samples. Some preliminary work on the effect of several different promoters was also included in this portion of the project. In the second area, particulate properties and ESP performance, the studies examined the effects of sorbent injection on the electrical resistivity and the particle size distribution of the ash. The use of flue gas conditioning and electrode modifications as potential remedial measures were examined, and computer projections of ESP performance with and without these measures were performed.

The sulfur capture studies and the in situ particulate measurements were performed in a 1.06 GJ/hr (1 x 10^6 Btu/hr) pilot-scale coal combustion facility at Southern Research Institute (SRI). The sulfur capture studies showed that hydrated lime was generally superior to limestone in terms of sulfur capture obtained at equivalent Ca/S ratios. Downstream injection was favored over near-flame injection for both sorbent types. With hydrated lime,. the optimum injection temperature was found to be about 1204°C (2200°F), where sorbent utilizations as high as 30% were achieved. Sorbent utilization was found to increase with decreasing particle size. In a size-fractionated LIMB ash sample from coal and hydrated lime, the sorbent utilization in 10-μm particles was about half of that in 1-μm particles. Preliminary studies with sodium- and lithium-based promoters showed significant enhancements with natural gas firing, but virtually no enhancement with coal firing.

The injection of either limestone or hydrated lime was found to remove most of the SO_3 in the flue gas, resulting in a high ash resistivity. With a medium-sulfur Indiana coal, the ash resistivity was increased by over two orders of magnitude when sorbent was injected. With limestone as the sorbent, it was found that SO_3 conditioning could be used to ameliorate the resistivity problem. Injection of about 30 ppm of SO_3 was sufficient to reduce the resistivity to a point where it would not limit electrical operation of the ESP. With hydrated lime injection, the efficacy of the SO_3 conditioning appeared to be sensitive to the sorbent injection conditions. This was attributed to differences in the degree of sulfation, which produces differences in SO_3 affinity in the reactive calcines from hydrated lime. Large increases in fine particle concentrations were also found when hydrated lime was injected. In general, it was concluded that some form of gas conditioning, possibly combined

with electrode modifications, would be required to maintain good electrical operating conditions during sorbent injection.

This report was submitted in fulfillment of Cooperative Agreement No. CR810012 by Southern Research Institute under the sponsorship of the U. S. Environmental Protection Agency. This report covers a period from July 1982 to July 1985.

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SECTION 1

INTRODUCTION

OVERVIEW OF THE ACID RAIN ISSUE AND THE LIMB PROCESS

It is well known that sulfur and nitrogen oxides are the major precursors of acid precipitation (U.S. Environmental Protection Agency. Acid Rain. EPA-600/9-79-036, July 1980. p. 5.). Coal-fired utility boilers account for approximately 70% of the sulfur oxide emissions and from 20 to 25% of the nitrogen oxide emissions in the United States. In that portion of the United States which is east of the Mississippi River, the 180,000 MW of installed coal-fired capacity account for about 16 million tons of SO_x and 4 to 5 million tons of NO_x emissions per year. Since only about 10% of these boilers are subject to emission controls for SO_x and NO_x under the New Source Performance Standards, it is apparent that any significant reduction of emissions will require retrofit of controls to the existing boiler population (1).

The Limestone Injection Multistage Burner (LIMB) process is potentially a low capital cost control technology which may be applicable to a significant number of existing wall-fired and tangentially-fired boilers. Although limestone injection alone may not achieve the original LIMB program goal of 50% SO_x reduction at a 2:1 Ca/S ratio, several other promising sorbents and process options have been identified by EPA's ongoing R&D program. Cost estimates of these process options indicate that injection of calcium-based sorbents in furnaces equipped with low NO_x burners shows substantial promise as a control technology for retrofit applications.

Considerable effort has been directed toward the optimization of sulfur capture in the LIMB process. This effort has included laboratory studies of the calcination and sulfation processes (2-4) as well as pilot-scale testing of various sorbents (5,6). The work that has been done to date has been successful in identifying sorbents and sorbent injection conditions that are capable of meeting the program goals of 50 to 60% SO_2 removal at a Ca/S ratio of 2:1. At this stage of development, however, neither the sorbent nor the process conditions can be said to be "optimized." There are also a number of unresolved questions concerning the economic constraints on the LIMB process; the effect of the process on boiler slagging, fouling, and reliability; and the effect of the process on particulate control equipment.

In a retrofit application, the LIMB process will produce a significant increase in the amount of particulate material that must be handled by the particulate collector. In most cases, the particulate collector will be an electrostatic precipitator (ESP) since ESPs currently service about 92% of the coal-fired electric generating capacity (7). The LIMB process may also alter the particle size distribution and the electrical resistivity of the particulate matter. These are two parameters that can play a critical role in precipitator performance. In addition to these key factors, a retrofit application of LIMB may also affect the operation of the ESP rapper system and the ash handling system. All of these effects must be studied and quantified in order to assess the effect of LIMB on ESP operation. Studies of these effects are also necessary to serve as a basis for making intelligent recommendations concerning potential corrective measures.

EPA's Air and Energy Engineering Research Laboratory is sponsoring a demonstration of LIMB technology at Unit No. 4 of the Edgewater Station of Ohio Edison Company. Testing of a LIMB process configuration on this 105-MW, wall-fired boiler is planned for the 1987-1988 time period. The final site-specific design for the Edgewater demonstration was completed in February of 1986.

OBJECTIVES AND SCOPE OF THIS STUDY

The research performed under this contract has been primarily directed toward the effect of LIMB on particulate characteristics and ESP performance. As part of this work, however, it has been necessary to evaluate the performance of various sorbents with respect to SO_2 capture. This work has included studies of SO_2 removal in coal flames and SO_2-doped natural gas flames using limestone, hydrated calcitic lime, pressure-hydrated dolomitic and calcitic lime, and promoted versions of these sorbents.

Our evaluations of sorbent performance have included the following elements:

(1) characterization of the coals in terms of proximate and ultimate analysis and ash composition;

(2) characterization of the raw sorbents in terms of chemical composition, surface area, pore size distribution, and particle size distribution;

(3) characterization of the calcined sorbents, produced under various conditions in the SRI combustor, in terms of chemical composition, surface area, pore size, particle size, and scanning electron microscope (SEM) and transmission electron microscope (TEM) examination;

(4) measurements of gas-phase SO_2 removal as a function of sorbent, injection location and rate, and time-temperature regime in coal flames and SO_2-doped gas flames in the SRI combustor;

(5) characterization of the sulfated calcines and ash/sorbent mixtures produced in the combustor, in terms of chemical composition, surface area, energy-dispersive X-ray analysis, electron spectroscopy for chemical analysis (ESCA), Auger electron spectroscopy (EAS), secondary ion mass spectrometry (SIMS), and electron microprobe analysis;

(6) measurements of the particle size distributions obtained with coal firing with and without sorbent injection at various locations in the combustor;

(7) fractionation of sulfated calcines and ash/sorbent mixtures into discrete particle size intervals, and determination of chemical composition and sorbent utilization as a function of particle size;

(8) examination of the effect of promoters on the performance of limestone and hydrated lime sorbents; and

(9) investigation of the effect of pressure hydration on the performance of calcitic hydrated limes.

The goal of the particulate and ESP work was to develop information that could be used to assess the probable effects of a LIMB retrofit on ESP performance, and suggest potential corrective measures to restore acceptable ESP performance. An assessment of this type requires data on the effect of sorbent injection on: the particle size distribution, the electrical resistivity, the ESP rapping requirements and reentrainment, and the operation of the ash handling system. The scope of this study was limited to the first two factors: particle size distribution and resistivity. Larger scale studies will provide the information concerning the effects on the rapping and ash handling systems.

One of the first major objectives of this study was to verify that the pilot combustor produced a fly ash that was an acceptable representation of that produced when the same coal was burned in a full-scale boiler. The characteristics of the fly ash produced in the pilot combustor were compared to the characteristics of fly ash from a full-scale (196-MW) boiler that was firing the same coal. This involved comparisons of the ash particle size distributions, electrical resistivities, morphologies, and chemical compositions. These comparisons, which are described in detail elsewhere (8), revealed excellent correspondence between the fly ashes from the pilot-scale combustor and the full-scale boiler. Thus, it was concluded that the ash simulation capabilities of the combustor were adequate for the follow-on studies with sorbent injection.

Cascade impactors, an optical counter, and an electrical aerosol size analyzer were used to make in situ measurements of the particle size distribution with and without sorbent injection. The effect of the sorbent injection on the electrical resistivity was determined from in situ measurements using a point-plane probe in the combustor flue gas at temperatures near 149°C (300°F). Laboratory resistivity measurements were also made using fly ash and ash/sorbent mixtures collected in a point-plane probe and equilibrated with simulated flue gas environments in the laboratory.

Larger-scale ESP work is planned, but will not be described here except to mention the major remaining elements of the LIMB particulate research program. A larger scale, ~85 m^3/min (~3000 ft^3/min), pilot precipitator test program is planned for 1986 using a modified version of EPA's mobile precipitator. Full-scale testing is also planned for 1987 at the Edgewater Station of Ohio Edison.

SECTION 2

STUDIES OF SULFUR CAPTURE IN THE LIMB PROCESS

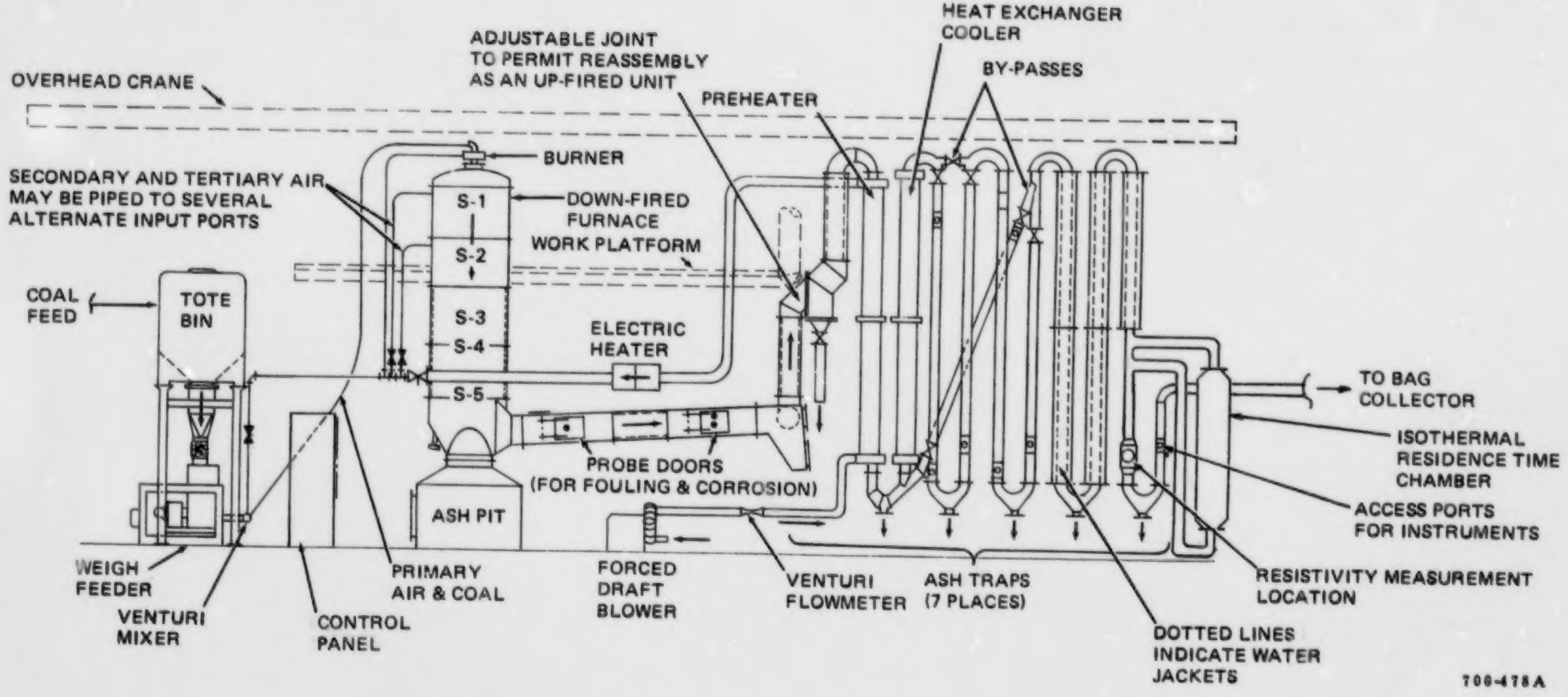
EQUIPMENT AND PROCEDURES

Pilot Combustion Facility

Figure 1 presents a schematic diagram of the SRI pilot-scale combustion research facility. The system includes a refractory-lined furnace which can fire either coal or natural gas at a rate of 0.63 to 1.27 GJ/hr (0.6 to 1.2 x 10^6 Btu/hr). The furnace is followed by both air- and water-cooled heat exchangers, and by a pulse-jet baghouse. A forced-draft and an induced-draft fan are used so that the system can be operated as a balanced draft unit. System design temperatures and gas velocities for the principal sections are given in Table 1.

The down-fired furnace is equipped with a modified version of EPA's Distributed Mixing Burner with outboard, tertiary air ports for staging. Sorbent injection points are located at the burner core and at seven locations between the burner and the outlet of the horizontal duct (see Figure 1). Both the coal and the sorbent are metered with Acrison gravimetric feeders. The sorbent may be aspirated into the primary air line for burner injection, or into a separate transport airstream for injection at other locations.

As shown in Figure 1, an isothermal residence chamber has been installed in the back-end of the system where the gas temperature is typically about 149°C (300°F). This chamber provides a gas residence time of about 1 sec in which the conditions are nearly isothermal. This simulates the time-temperature interval between the air heater and the ESP in a power plant. The simulation of this part of the ash thermal history is critical to the uptake of SO_3 and its effect on resistivity. The sampling port for the particle size and resistivity measurements is located just downstream from the isothermal residence chamber. The effect of SO_3 conditioning may be studied using a conditioning system that has been installed upstream of the isothermal residence chamber. This system consists of an electrically heated catalytic reactor and injection line. Sulfur dioxide is metered from a gas cylinder and passes through the catalytic reactor where it is converted to SO_3. The resulting SO_3 is then injected into the flue gas at a point upstream of the residence chamber to allow adequate mixing and sufficient time for uptake on the particulate.



OVERHEAD CRANE
ADJUSTABLE JOINT TO PERMIT REASSEMBLY AS AN UP-FIRED UNIT
PREHEATER
HEAT EXCHANGER COOLER
BY-PASSES
BURNER
SECONDARY AND TERTIARY AIR MAY BE PIPED TO SEVERAL ALTERNATE INPUT PORTS
S-1
DOWN-FIRED FURNACE
WORK PLATFORM
S-2
COAL FEED
TOTE BIN
S-3
S-4
ELECTRIC HEATER
S-5
TO BAG COLLECTOR
ISOTHERMAL RESIDENCE TIME CHAMBER
PROBE DOORS (FOR FOULING & CORROSION)
ASH PIT
ACCESS PORTS FOR INSTRUMENTS
WEIGH FEEDER
PRIMARY AIR & COAL
FORCED DRAFT BLOWER
VENTURI FLOWMETER
ASH TRAPS (7 PLACES)
RESISTIVITY MEASUREMENT LOCATION
VENTURI MIXER
CONTROL PANEL
DOTTED LINES INDICATE WATER JACKETS
700-478A

Figure 1. Pilot Plant used for sulfur capture and particulate characterization studies. (S-1, 2, 3, 4, 5, refer to ports for sorbent injection or sampling.)

TABLE 1. SYSTEM DESIGN TEMPERATURES AND GAS VELOCITIES

	Average gas temp (°C [°F])	Average velocity (m/sec [ft/sec])
Furnace	1621-1149 [2950-2100]	1.3 [4.2]
Simulated superheater/reheater	1149-943 [2100-1730]	7.0 [23]
Refractory-lined water jacket	943-829 [1730-1525]	20.1 [66]
Air preheater	829-477 [1525-890]	10.7 [35]
Heat exchanger No. 2	477-313 [890-595]	9.4 [31]
Air-cooled loops	313-183 [595-362]	18.3 [60]
Water-cooled loops	183-127 [362-260]	16.8 [55]

Continuous Flue Gas Analyzers

During furnace tests of the sorbents, the furnace flue gas is continuously monitored for SO_2, NO_x, CO_2, and O_2. The flue gas is extracted from the combustor system ductwork at a point where the gas temperature is about 204°C (400°F). A sintered stainless steel probe is used to separate the entrained particles and provide a clean gas flow to the conditioning system. The buildup of a filter cake on the probe is minimized by operating at a very low face velocity (~0.71 cm/sec or 1.4 ft/min) with a flue gas velocity on the order of 18.3 m/sec (60 ft/sec). The ability of the probe to sample flue gas without loss of SO_2 has been demonstrated by tests conducted with known levels of SO_2 injected just ahead of the probe while sorbent was injected at various furnace locations.

After the flue gas is extracted through the sintered stainless steel probe, the clean gas is drawn through a heated Teflon sample line to a Thermo-Electron Model 600 Conditioning System. In the conditioning system, the gas sample is drawn through two condensers and an additional particle filter before being routed to the continuous gas analyzers. Analysis of the condensate collected in the conditioning system has shown that loss of SO_2 to the condensate is insignificant.

DuPont Model 400 Ultraviolet SO_2 Analyzer--

The SO_2 level in the flue gas is monitored by a DuPont Model 400 Ultraviolet Photometric SO_2 Analyzer. This same instrument is currently used for monitoring SO_2 at many power plants throughout the United States. The analyzer operation is based upon the ultraviolet absorption of the SO_2 molecule. The measuring wavelength (280 nm) is strongly absorbed by SO_2 while the reference wavelength (577 nm) is not. Any interference from NO_2 is eliminated since NO_2 absorbs both wavelengths to the same extent. There are no interference problems with any other common stack gas constituents or particles.

ThermoElectron Model 10 Chemiluminescent NO_x Analyzer--

For monitoring flue gas NO_x concentrations, a ThermoElectron Model 10 Chemiluminescent Analyzer is used. In this analyzer, ozone is generated from dried air and then combined with the flue gas sample in a reaction chamber where the NO in the sample reacts with the ozone to form excited NO_2. The excited NO_2 then decays to its ground state giving off a photon of energy. The emitted radiation is monitored on a photomultiplier tube and provides a sensitive measure of the level of NO in the flue gas sample. The analyzer can be operated in two different modes to determine both NO and total NO_x. To determine total NO_x, the NO_2 is first thermally converted to NO at 700°C and then reacted with O_3 as described above. By alternately passing the sample through the NO_2 to NO converter, it is possible to obtain separate measures of NO and total NO_x (NO + NO_2). It is assumed that the amount of N_2O in the sample is negligible.

Beckman Model 864 Nondispersive Infrared CO_2 Analyzer--

The continuous CO_2 analyzer used in this project is a Beckman Model 864 Nondispersive Infrared Analyzer. This analyzer uses a chopped beam of infrared radiation which is passed through both the sample cell and a reference cell containing a nonabsorbing gas. The difference in transmitted infrared radiation through the two cells is the energy absorbed by the CO_2 and is converted to a CO_2 concentration.

Beckman Model 755 Paramagnetic O_2 Analyzer--

A Beckman Model 755 Paramagnetic Analyzer is used to measure flue gas oxygen levels. The instrument measures the magnetic susceptibility of oxygen. A test body is mounted on a platinum suspension in a nonuniform magnetic field. The magnetic force exerted upon the test body is proportional to the difference in the volume magnetic susceptibilities of the test body and the surrounding gas. If the gas is more paramagnetic than the test body, the magnetic force tends to repel the test body; if the gas is less paramagnetic, the magnetic force tends to move the test body into the magnetic field.

A diamond-shaped mirror mounted on a platinum suspension wire reflects light from a prefocused light source equally onto two photocells when the test body is in the neutral position. When the volume magnetic susceptibility of the gas increases, a magnetic force is applied to the test body tending to rotate it out of the field. The suspension mirror on the test body also rotates so that the photocells become unequally illuminated and, through an amplifier, apply feedback current to the test body. The electromagnetic force generated by the feedback current is opposite and almost equal to the magnetic force. This current is a linear function of the oxygen concentration. The effect of this current is converted to an output that may be recorded for a permanent record of oxygen concentration. The magnetic susceptibility of flue gas is almost totally due to the oxygen, so interferences are negligible.

Description of Procedures Used to Evaluate Sorbent Performance

This section describes the two types of sorbent evaluation tests carried out with the pilot-scale combustor: those in which only the gas-phase reduction of SO_2 with the introduction of sorbent during coal-firing was determined; and those in which solids samples were collected during gas firing for further characterization.

Reduction of Gas-Phase SO_2--

The standardized test chosen to evaluate a large number of variables on the basis of overall SO_2 removal was the following: 1) establish steady state at the conditions of interest; 2) begin feeding sorbent to the sorbent eductor; 3) terminate sorbent addition after 10 min. Table 2 gives the definitions used for reporting calcium-to-sulfur ratio, SO_2 reduction, and calcium utilization.

The gas sampling system has been shown to make no contribution to the reduction of SO_2. That the contribution of deposited sorbent to the overall reduction is minor is inferred qualitatively from the similar response of the system either to sorbent initiation or to reduction in SO_2 feed. Analysis of solid samples has in general confirmed the apparent utilization calculated from gas composition.

TABLE 2. MEASURED VALUES USED TO CALCULATE SO_2 REDUCTION AND CALCIUM UTILIZATION

Calculated value	Measured values
Ca/S	- Sorbent feed rate - Typical sorbent analysis - Molar flue gas rate (from fuel rate and analysis) corrected to 3% O_2 - Baseline SO_2
Baseline SO_2 (ppm)	- Average value of SO_2 in 5-min period preceding test, corrected to 3% O_2
Reduced SO_2 (ppm)	- Average value of SO_2 over period 2 to 10 min after starting sorbent feed, corrected to 3% O_2
SO_2 Reduction (%)	$- 100 \left(1 - \frac{\text{reduced } SO_2}{\text{baseline } SO_2}\right)$
Calcium utilization (%)	$- \frac{SO_2 \text{ reduction}}{\text{Ca/S}}$

Solids Sampling--

Solids samples are withdrawn from the furnace through a water-cooled probe and collected in a glass-fiber thimble at the probe exit. The central sample tube is separated from the coolant by an annulus through which diluent may be added to the sample at the probe entrance. Initial experiments showed that in-probe reaction of calcine sampled either with or without dilution resulted in no more than 1 to 2% each of H_2O, CO_2, or SO_x in the solid. Thus, the sampling procedure adopted for this study was to sample undiluted flue gas while maintaining the cooling water exit temperature at 54°C (130°F) and the collecting filter at 149°C (300°F) to avoid condensation.

Subsequent to these initial probe validation tests, much more reactive calcines were encountered. Injection of high-calcium or dolomitic hydrated lime in the lower furnace, for example, yields calcines with surface areas of 10 to 15 or 30 to 40 m^2/g (compared to 2 to 3 m^2/g for the calcine from burner injection of limestones in the tests cited above). With these calcines, $Ca(OH)_2$ and $CaCO_3$ each account for 5 to 20 mol % of the total calcium. The reactions to hydroxide and carbonate are assumed to occur in the probe since the temperature in the furnace is well above the decomposition temperature of either.

Figure 2 shows the potential for in-probe reaction of SO_2 with the most reactive calcine tested (9). In these tests, calcine was sampled during injection of dolomitic hydroxide at S-4. One series was completed with SO_2 added to the gas flame (normal sampling). A second series was then completed with no SO_2 added to the flame, but with SO_2 added to the inlet of the probe. Any sulfate present in the second series of samples had to be due to reaction within the probe itself. At the level of injection, the in-probe reaction is equivalent to the overall reaction when SO_2 is present in the furnace (normal sampling). Clearly, this sampling procedure gives no information on the extent of in-furnace sulfation at the level of injection. Although it appears that in-probe reaction could account for as much as 30% of the utilization measured at S-5 and SD-2, such is not likely the case. When SO_2 is present only in the probe, the reaction is with "fresh" calcine, and represents only an upper limit in additional in-probe reaction of sulfated calcine. The agreement between solids analysis and exit SO_2 reduction (measured at about 371°C (700°F), as described previously) supports the idea that additional reaction in the probe is much less.

Neither elevation of the filter temperature to 260°C (500°F) nor use of air rather than water as a probe coolant appeared to make a consistent difference in calcine BET area or composition. While work continues on the development of a better sampling technique, the present results are thought to be deficient only for the most reactive calcines.

Furnace Temperature Measurements--

These measurements were made with a suction pyrometer, or high-velocity thermocouple (HVT). The pyrometer was built in-house and is shown in Figure 3. Combustion gas is drawn through the annulus formed by a thermocouple and its radiation shield. The approach to true gas temperature is determined by the

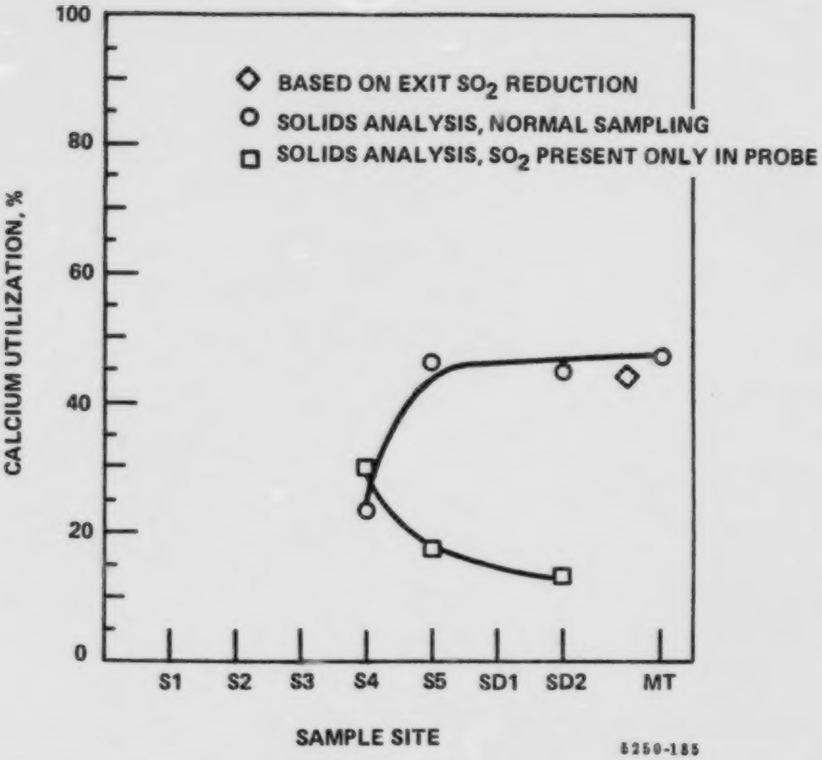


Figure 2. Calcium utilization for dolomitic pressure-hydrated lime injected at S-4 with gas firing: in furnace compared to potential in-probe reaction. "MT" is a mass-train sampled isokinetically at about 149 °C (300 °F). (Taken from Reference 9.)

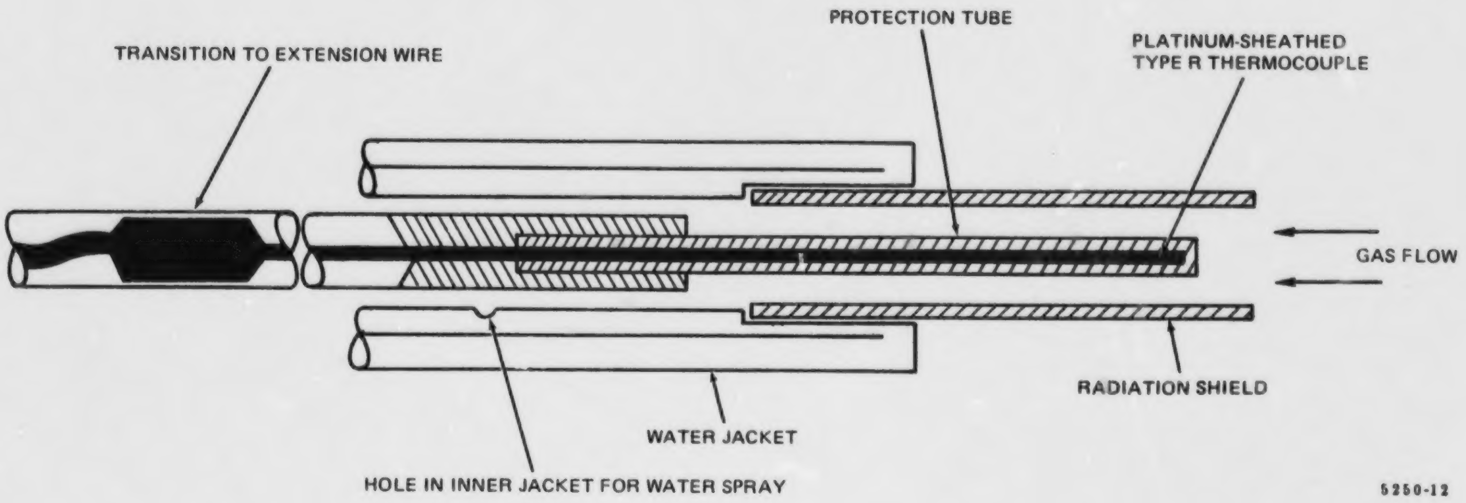

PROTECTION TUBE
TRANSITION TO EXTENSION WIRE
PLATINUM-SHEATHED TYPE R THERMOCOUPLE
GAS FLOW
RADIATION SHIELD
WATER JACKET
HOLE IN INNER JACKET FOR WATER SPRAY
5250-12

Figure 3. Suction pyrometer.

gas velocity, which enhances convective heat transfer to the thermocouple, and the shield design, which decreases radiative loss to the combustor walls. The only unusual feature of the probe is that a water spray is used to cool the gas after it enters the probe, allowing a platinum-sheathed thermocouple of reasonable length to be employed (the transition to extension wire must be at less than 204°C (400°F). A ceramic protection tube prevents slag from sticking to the thermocouple. This design makes the probe quite robust. The suction flow rate exceeds the value recommended by Steam for HVT operation (10).

Figure 4 shows three shield configurations tested. Unshielded, the pyrometer is equivalent to a simple thermocouple (the normal practice of testing temperature versus suction rate is not possible because of the water spray). The single-shield configuration is normally used in gases containing ash. The multiple shield is made by placing hollow tubes in the single-shield annulus. Figure 5 shows temperatures measured at three levels in the furnace (gas fired). At the upper limit of use of the probe (thermocouple rated to 1650°C [3002°F] maximum) the single-shield measurement is within 5% of the multiple shield, whereas unshielded, the deviation is 12%.

The temperature measured with the multiple shield in the furnace during coal firing was initially higher than that with the single shield (1150 versus 1120°C or 2102 versus 2048°F) but decreased rapidly to 1110°C (2030°F). The decrease in centerline temperature over the 15-min interval required for a furnace traverse is typically 5 to 30°C (41 to 86°F) using the single shield. For this reason, and ease of use, the single-shield configuration was used to measure temperature profiles during coal combustion.

Test procedure--For each firing condition, a horizontal traverse in each furnace section was performed as follows: (1) Locate the probe at the center of the furnace and record the maximum temperature reached. Usually the temperature reaches a peak and then decreases slowly. (2) Advance the probe in 5.0-cm (2-in.) increments, recording the temperature at each point. (3) Return to the center position and note temperature. (4) Withdraw the probe in 5.0-cm (2-in.) increments. (5) Return to the center position and note the final temperature. This procedure provides an estimate of the error due to ash buildup in the probe.

A traverse of each of five furnace sections was made for each firing condition. Entry was always made from the west wall of S-1 through S-4 and from the south wall of S-5. For some conditions, the furnace was traversed from both south and west walls and the symmetry was good. Table 3 lists the distance of each section's port from the burner exit.

Combustor temperature characterization--Radial temperature profiles are shown in Figures 6 and 7 for firing rates of 1.06 and 0.636 GJ/hr (1.0 and 0.6 x 10^6 Btu/hr). Each figure shows a traverse at every port for coal firing, and near-burner profiles for gas firing. Note that firing with gas gives much higher temperatures near the burner than does coal. The difference is especially pronounced with the lower firing rate. Temperatures with either fuel are similar downstream of the burner.

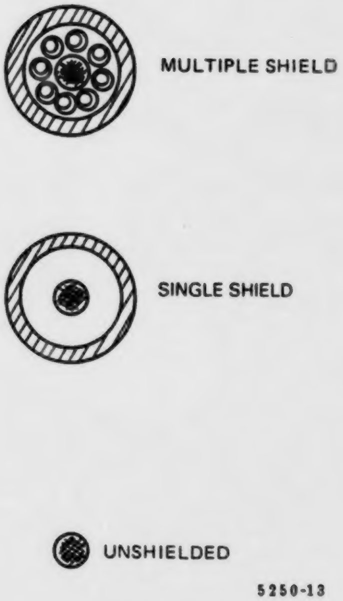


Figure 4. Suction pyrometer shield configurations.

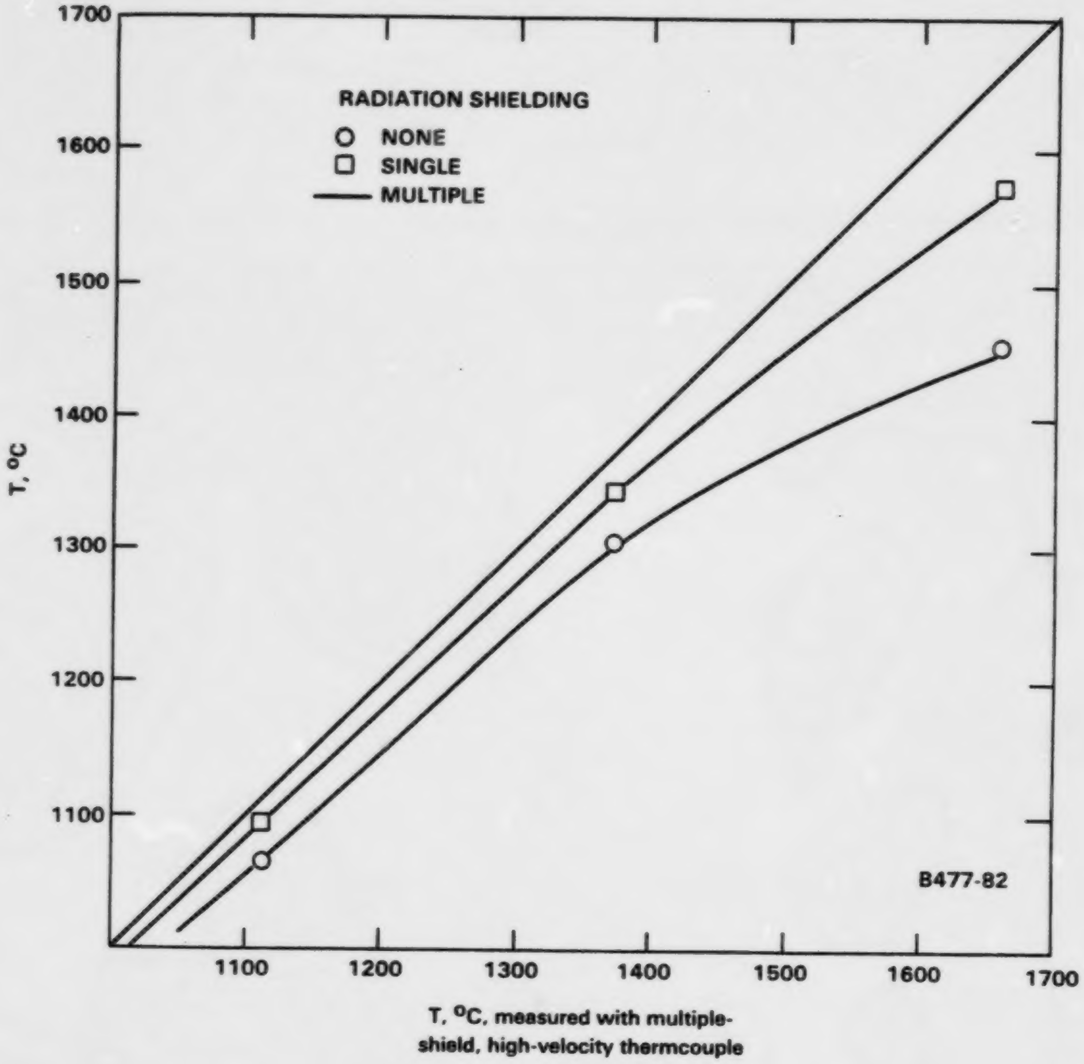


Figure 5. Performance of high-velocity thermocouple with no, single and multiple radiation shields with gas firing.

TABLE 3. PORT LOCATIONS FOR BURNER TEMPERATURE MEASUREMENTS AND STAGING

	Section	Distance from burner, m (ft)
Pyrometer probe:		
	1	0.229 (0.75)
	2	0.838 (2.75)
	3	1.524 (5.0)
	4	2.286 (7.5)
	5	3.018 (9.9)
Axial staging:	Four 5.0-cm (2-in.) diameter ports parallel to burner axis, located on a 33.02-cm (13-in.) radius from the center of the combustor.	
Radial staging:	Four 5.0-cm (2-in.) diameter ports perpendicular to burner axis, located 0.58 m (1.92 ft) below burner	

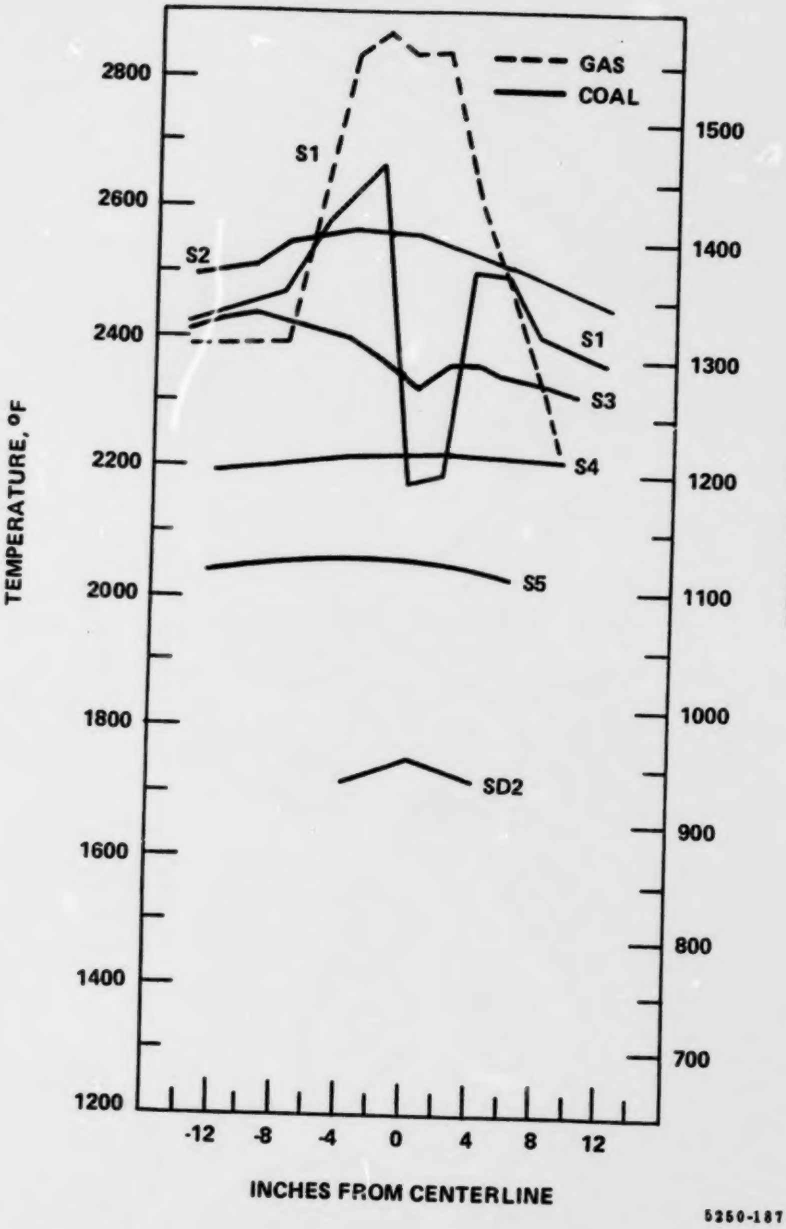


Figure 6. Radial temperature profiles at 1.06 GJ/hr (1 x 10^6 Btu/hr).

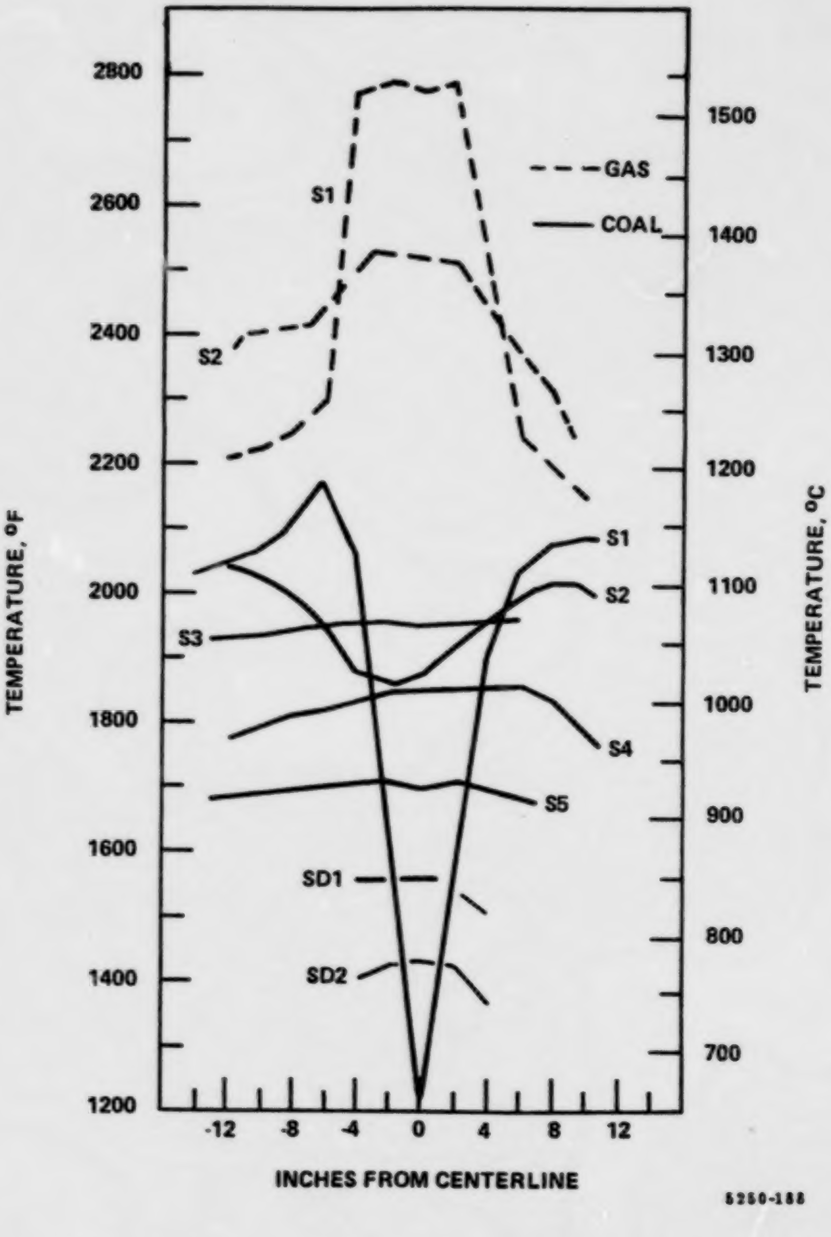


Figure 7. Radial temperature profiles at 0.636 GJ/hr (0.6 x 10^6 Btu/hr).

The profiles shown in Figures 6 and 7 were taken with an adjustable-swirl burner operated without staging of combustion air. Considerable work under this project was performed with a version of EPA's Distributed Mixing Burner (DMB) constructed for this purpose. The DMB was typically operated with tertiary or staging air added outboard of the burner proper through four ports parallel to the burner axis. Testing on this and related projects established that sorbent performance is primarily a function of injection temperature rather than combustion stoichiometry. Furthermore, optimum sorbent performance was achieved with injection away from the burner, where near-burner temperature variations due to burner design are irrelevant. Therefore, the profiles shown in Figures 6 and 7 may be taken as typical for the combustor at high and low load. The temperature at a particular level can vary with the condition of the combustor walls, and is normally measured in conjunction with specific tests.

FUELS AND SORBENTS

Coal Types and Characteristics

Three different batches of an Indiana (Buffaloville seam) coal, three batches of the Jefferson County, Alabama, Hallmark coal, and one batch of the Illinois (Freeman No. 6 seam) coal were used in this work. Typical proximate and ultimate coal analyses are given in Table 4, and typical ash compositions are listed in Table 5. The first batch of the Indiana coal was found to be too high in sulfur and iron content compared to the batches of Indiana coal being used by other EPA contractors, so only limited testing was done with the first batch. The last batch of Indiana coal (~40 tons) was somewhat higher in sulfur, ash, and moisture than the previous batch, which was exhausted in February 1984. There was also some difference between the three batches of Hallmark coal as indicated in the table. The ash compositions for the two batches were generally quite similar however. The very low calcium content of the coal minimizes the complication of SO_2 removal by the calcium in the ash.

Sorbent Types and Characteristics

Five different sorbents have been used in SRI's LIMB research program: (1) a high-calcium limestone, Vicron 45-3 limestone, in a prepulverized form supplied by Union Carbide Corporation; (2) a commercial limestone, designated "Marianna fine;" (3) a high-calcium hydrated lime obtained from the Longview Plant of Dravo Lime Company; (4) a high-calcium hydrated lime obtained from the Pelican Lime Plant of Dravo; and (5) a dolomitic pressure-hydrated (P-H) lime obtained from the Corson Lime Company. The properties of these sorbents are summarized in Table 6. The loss on ignition (LOI) reflects the weight loss associated with the CO_2 or H_2O driven off, and the remainder of the chemical analysis refers to the ignited, or decomposed, material.

Characterization of Calcined Sorbents--

The five sorbents discussed above have been calcined in the SRI pilot combustor and in the laboratory, and the calcines have been studied in terms of their chemical composition, surface area, pore size, and particle size, and

TABLE 4. PROXIMATE AND ULTIMATE COAL ANALYSES[a]

	Indiana Batch 1	Indiana Batch 2	Indiana Batch 3	Hallmark Batch 1	Hallmark Batch 2	Hallmark Batch 3	Illinois
Proximate							
% Moisture	6.4-8.9	10.6-11.5	15.4-16.0	1.9	2.2	1.6	5.4-11.7
% Ash	7.9-11.9	7.1-8.0	8.7-9.7	7.7	7.7	8.3	6.7-7.4
% Volatile	37.3	32.1-32.7	32.9	37.2	--	37.0	30.7-34.7
% Fixed carbon	44.6	48.7-49.5	42.0-42.3	53.2	--	53.1	50.8-53.4
Btu/lb	11,500-12,200	11,100-11,300	10,900-11,100	13,500	13,400	13,400	11,800-12,600
% Sulfur	3.5-4.3	1.9-2.1	2.6-2.7	3.4	2.9	3.9	1.6-2.0
Ultimate							
% Moisture	6.4-8.9	10.6-11.5	15.4-16.0	1.9	2.2	1.6	5.4-11.7
% Carbon	63.4-67.2	64.2-64.9	61.3-61.8	74.1	--	73.9	66.0-71.3
% Hydrogen	4.4-4.7	4.0-4.1	3.9-4.0	5.2	--	4.8	5.1-5.5
% Nitrogen	1.2-1.3	1.2	1.1-1.2	1.7	--	1.6	1.3-1.4
% Chlorine	0.2-0.2	0.05-0.06	0.04	ND[b]	--	0.06	ND
% Sulfur	3.5-4.3	1.9-2.1	2.6-2.7	3.4	--	3.9	1.6-2.0
% Ash	7.9-11.9	7.1-8.0	8.7-9.7	7.7	--	8.3	6.7-7.4
% Oxygen[c]	6.7-7.9	9.4-9.8	5.7-5.8	5.9	7.7	5.9	7.1-7.6

a. As-received basis.

b. Not determined.

c. Oxygen by difference.

TABLE 5. ASH COMPOSITIONS[a]

	Indiana Batch 1	Indiana Batch 2	Indiana Batch 3	Hallmark Batch 1	Hallmark Batch 2	Hallmark Batch 3	Illinois
% Li_2O	ND[b]	0.03	0.03	0.04	0.04	0.03	0.02
% Na_2O	0.65	0.10	0.15	0.25	0.41	0.46	1.7
% K_2O	1.3	0.64	0.70	1.5	1.5	1.4	1.1
% MgO	0.81	0.31	0.49	0.69	0.71	0.56	0.88
% CaO	1.8	2.1	1.5	1.1	1.4	1.3	1.8
% Fe_2O_3	37.5	25.9	24.0	45.9	38.6	54.3	19.5
% Al_2O_3	19.1	24.7	25.2	17.2	20.9	14.5	22.0
% SiO_2	34.6	41.8	45.9	28.7	33.5	25.0	47.0
% TiO_2	0.80	1.3	1.5	1.0	1.5	1.1	1.5
% P_2O_5	0.30	0.15	0.13	0.56	0.66	0.27	0.57
% SO_3	1.3	1.6	0.87	1.1	0.33	0.31	1.0
% LOI[c]	ND	1.6	1.7	ND	ND	ND	1.0

a. Weight percent of the element expressed as the oxide.

b. Not determined.

c. Loss on ignition at 750°C (1382°F).

TABLE 6. CHEMICAL COMPOSITIONS, MEDIAN PARTICLE SIZES, AND SURFACE AREAS OF RAW SORBENTS[a]

	Vicron 45-3 limestone $(CaCO_3$	Marianna limestone $(CaCO_3)$	Longview hydrated lime $(Ca(OH)_2)$	Pelican hydrated lime $(Ca(OH)_2)$	Corson pressure-hydrated dolomitic lime $(Ca(OH)_2 \cdot Mg(OH)_2)$
% Li_2O	0.01	0.02	0.02	ND[d]	0.01
% Na_2O	0.03	0.07	0.02	0.11	0.03
% K_2O	0.03	0.18	0.08	0.17	1.18
% MgO	0.80	1.2	3.0	5.5	38.9
% CaO	98.7	90.6	93.9	91.9	55.1
% Fe_2O_3	0.16	1.2	0.30	0.23	1.67
% Al_2O_3	0.20	1.7	0.43	0.50	0.44
% SiO_2	0.10	4.8	0.51	2.2	3.9
% TiO_2	<0.10	<0.10	<0.10	<0.30	<0.10
% P_2O_5	0.05	0.25	<0.13	<0.03	<0.02
% SO_3	0.03	0.28	0.27	0.32	0.08
% LOI	43.7	42.2	23.7	23.5	26.1
Median particle size, μm	15	13	2.3	2.0	1.3
Surface area, m^2/g	0.82	6.3	16.6	13.0	18.6

a. All values, except for LOI, median particle size, and surface area, pertain to ignited material.

b. Not determined.

they have been examined under the SEM and the TEM. The degree of calcination is established by a CHN analysis which allows the carbonate and hydroxide content of a calcine to be calculated. When the calcination is complete, the chemical analyses generally agree quite well with the results obtained on the ignited samples.

Filter samples of calcined Vicron which were collected at the resistivity port of the SRI combustor (refer back to Figure 1), where the gas temperature is typically about 149°C (300°F), have shown BET surface areas in the range of 4.0 to 4.2 m^2/g, whereas the same material shows an area in the range of 3.0 to 3.6 m^2/g after sulfation at a Ca/S mole ratio of 2:1 (about 35% SO_2 capture or 17% utilization). Slightly higher surface areas were obtained at low load, but the major differences were noted when samples were collected at locations closer to the point of injection. Samples collected at S-5 and S-2 (see Figure 8), where the gas temperatures were about 927°C (1700°F) and 1149°C (2100°F) at low load, had surface areas of 5.2 and 7.3 m^2/g, respectively. The latter value is the highest surface area that has been measured for a Vicron calcine produced in the SRI furnace. Burner injection of the Marianna limestone resulted in a continuous decline in surface area from the point of injection. Injection at S-4, however, produced a peak area about twice that of the raw limestone. Even higher surface areas were produced by injection at low load (0.636 GJ/hr or 0.6 x 10^6 Btu/hr).

The Longview hydrated lime produced a calcine with a generally higher surface area than that produced from the limestone. When the hydrated lime was injected at S-4 and samples of the calcine were collected at various points downstream, the following data were obtained: 15.6 m^2/g at S-4 (~1204°C or 2200°F), 9.8 m^2/g at the first sampling port in the horizontal duct (~1093°C or 2000°F), and 8.3 m^2/g at the resistivity port (~149°C or 300°F). This suggests that the surface area of the Longview calcine decreases monotonically from the point of injection from its initial value of 16.6 m^2/g for the raw material to a value that is half of that at 149°C (300°F). The surface area of the Vicron calcine, on the other hand, goes through a maximum value near the injection point that is much higher than the surface area of the original stone, but still lower than the surface area of the calcined hydrate.

In experiments with the pressure-hydrated dolomitic lime, calcine surface areas as high as 45 m^2/g have been measured with samples collected at S-5 when the injection is at S-4. Calcination at lower temperatures in the laboratory has produced even higher surface areas as illustrated in Figure 9. This shows the effect of heating a sample of the raw material at a constant temperature of 300°C (572°F) over a period of 12 hr under an atmosphere of N_2 and He in the BET apparatus. The surface area of the calcine produced from the pressure hydrate increases dramatically until reaching a final value of over 100 m^2/g after 12 hr. The surface areas of the Longview hydrate and a pressure-hydrated calcitic lime obtained from the University of North Dakota Energy Research Center did not change upon heating them at 300°C (572°F). This would not be true at higher temperatures.

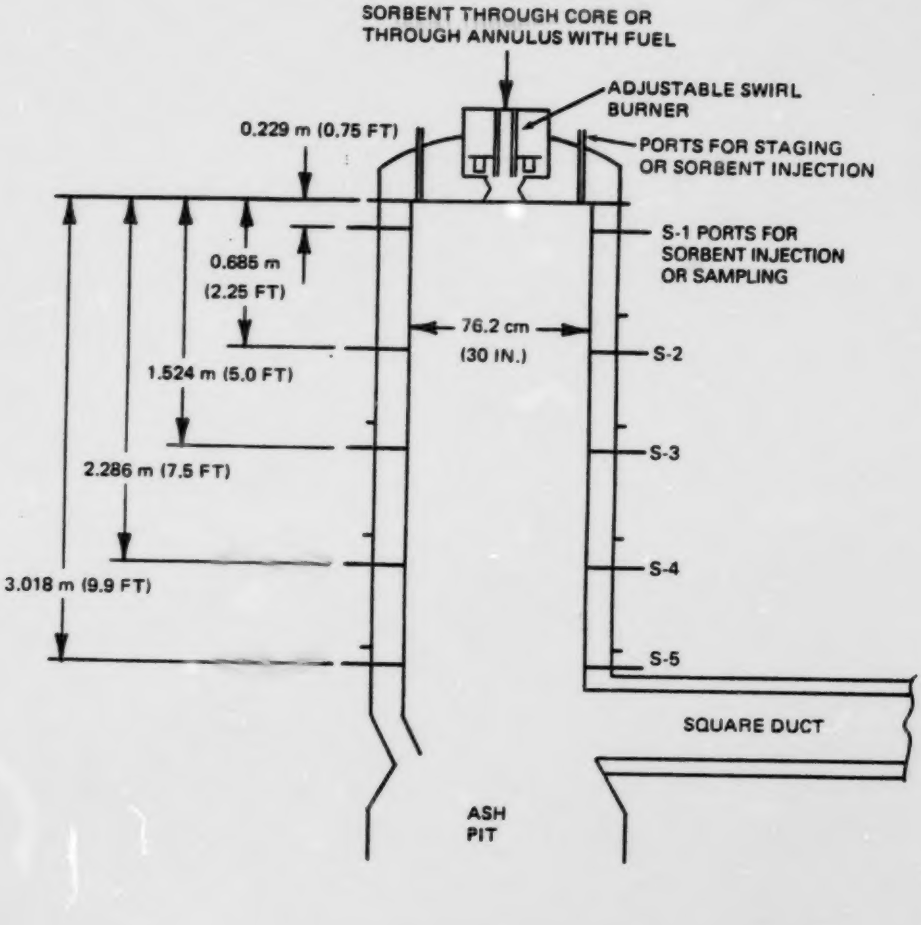


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Figure 8. Furnace of pilot-scale combustor.

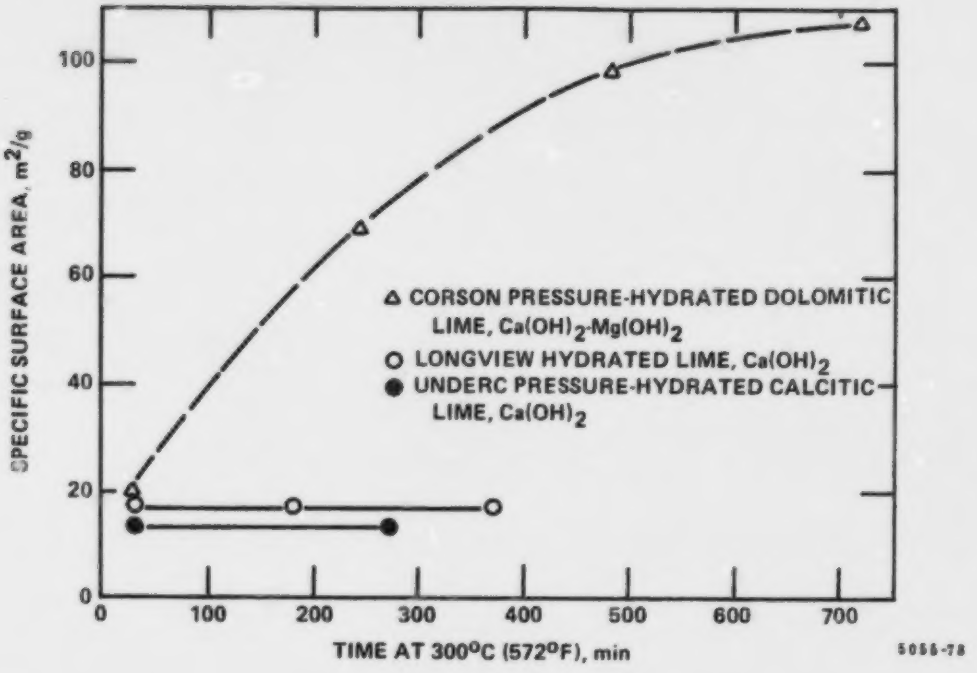

Figure 9. Effect of conditioning time at 300 °C (572 °F) on the surface area of hydrated limes.

The mercury intrusion "pore" volumes of the various calcines have been determined, but the results must be considered in light of the uncertainties associated with distinguishing pores and interparticle voids. Problems caused by crushing the sample at high mercury pressures must also be identified and taken into account. The values obtained with the various sorbents injected at S-4 and sampled at S-5 (without correction for the effects of voids and deformation) are as follows:

Vicron limestone	0.71 cc/g
Longview hydrated lime	2.09 cc/g
Corson pressure-hydrated lime	1.35 cc/g

The Corson calcine apparently yields less pore volume than the ordinary hydrate, although the pressure hydrate yields a higher surface area. This suggests that the pores are smaller in the pressure hydrate, the difference being roughly a factor of four. The average pore sizes, without correction for voids or particle deformation effects, are 1300 and 300 Å for the Longview and Corson calcines. Correcting for void effects by using the area median pore diameters, these values for the calcined Longview hydrate are 300 Å by nitrogen adsorption and 50 Å by mercury intrusion.

It is interesting to note that examination of limestone calcines under the SEM shows that the porosity is not in the form of well-defined cylindrical pores, but rather in a form that is closer to a slit geometry. Examination of a limestone calcine produced at EPA showed that the slits were on the order of 100 Å in width and up to several microns in length. The slits appeared to be predominant on one face of the calcined limestone particle, suggesting that the calcination proceeded in a direction determined by the crystallographic orientation or the grain boundaries in the stone.

Calcined Vicron limestone that was collected in the baghouse of the SRI combustor while firing natural gas was found to have a median (Bahco) particle size of about 5 μm with about 6% of the calcine in the submicron range. This is to be compared to the raw stone which has a median size of 12.5 μm by Bahco (or 15 μm by sedimentation) with less than 2% below 1 μm. The shift in mean size may be partially due to dropout in the system, but the large increase in submicron particles can only be explained by decrepitation of the stone as it was calcined in the furnace. Cascade impactor measurements of the size distribution of calcined Vicron limestone have shown that the submicron particulate concentration contributed by the sorbent is about 300 mg/dnm^3 (0.131 gr/dscf). This was found to be comparable to the submicron loading of fly ash produced from a fine grind of a South African coal used for initial combustor tests.

Cascade impactor measurements performed with the Corson pressure-hydrated dolomitic lime suggest that between 40 and 70% of the calcine is smaller than 2 μm in size. This is much finer than the calcine produced from the Vicron limestone. Although most of the calcine area is internal area, finer particles of calcine may be advantageous from the standpoint of minimizing the distance that the SO_2 must diffuse to penetrate deep into the particle. However, particles that are too fine may pose an unmanageable particulate collection problem.

MEASUREMENT OF GAS-PHASE SO_2 REMOVAL

Screening Studies of Sorbent Type and Injection Location

With the Indiana Batch No. 3 coal being fired at full load, the sulfur capture was evaluated with three different sorbents injected at locations ranging from the burner to S-4 (flame to 1121°C or 2050°F). Each of the following sorbents was evaluated at Ca/S mole ratios of 0.5 to 4.0:

Vicron 45-3 limestone, $CaCO_3$,
Longview hydrated lime, $Ca(OH)_2$, and
Corson pressure-hydrated dolomitic lime, $Ca(OH)_2$-$Mg(OH)_2$.

All of the above testing was done during staged combustion of the Indiana Batch No. 3 coal. The burner and tertiary air rates represented 73 and 62% of the theoretical air requirement. The firing rate was 36.3 kg/hr (80 lb/hr) or about 1.06 GJ/hr (1×10^6 Btu/hr).

The Marianna limestone and the Pelican hydrated lime were evaluated by S-4 injection of the sorbents while firing the Hallmark Batch 1 coal. The data on these tests are discussed later.

The results of the Vicron limestone, Longview hydrated lime, and Corson pressure-hydrated lime tests are summarized in Table 7. The results show that downstream injection at S-3 or S-4 was superior to burner injection for the Vicron limestone and the Longview hydrated lime. Therefore, burner injection of the Corson pressure-hydrated (P-H) lime was not attempted since the amount of this material was limited. The best results were obtained with the Corson P-H lime injected at S-3. This gave a sulfur capture of 80.6% at a Ca/S mole ratio of 2:1. Of course, the magnesium content is not reflected in the Ca/S ratio.

Figure 10 shows the sulfur capture data obtained with Vicron 45-3 limestone with the Indiana Batch No. 3 coal. With Vicron limestone, the sulfur removal is surprisingly insensitive to the injection location or gas temperature. Also the sulfur removal is generally poor with Vicron limestone regardless of where it is injected in the furnace system.

Figure 11 shows the sulfur capture data obtained with Longview hydrated lime with the Indiana Batch No. 3 coal. The sulfur capture obtained with Longview hydrated lime is obviously more sensitive to the injection location than that obtained with Vicron limestone. The Longview hydrated lime also gives better results than Vicron limestone at all injection locations. The optimum injection location appears to be S-3, where the maximum gas temperature is about 2260°F.

Figure 12 shows the sulfur capture data obtained with Corson P-H dolomitic lime with the Indiana Batch No. 3 coal. Due to the limited amount of this material that was available, tests were done at only one injection location. The selected injection site was S-3 since this gave the best SO_2 removals with

TABLE 7. SUMMARY OF SULFUR REMOVAL DATA OBTAINED WITH THREE DIFFERENT SORBENTS WITH THE INDIANA BATCH NO. 3 COAL

Run No.	Sorbent[a]	Injection location[b]	Ca/S ratio (mole/mole)	Sulfur capture (%)
C482-14	V	B	2	33.6
C482-15	V	B	1	21.7
C482-16	V	B	4	53.7
C482-17	V	B	4	63.2
C482-20	V	B	2	36.9
C482-35	V	B	2	35.4
C482-36	V	B	4	55.7
C482-23	V	S-3	2	38.4
C482-24	V	S-3	1	23.8
C482-25	V	S-3	4	57.9
C482-26	V	S-3	2	39.1
C482-28	V	S-4	2	33.3
C482-29	V	S-4	1	19.7
C482-30	V	S-4	2	32.8
C482-31	V	S-4	4	54.9
C482-43	L	B	2	35.5
C482-45	L	B	1	25.5
C482-46	L	B	4	50.4
C482-47	L	B	2	38.6
C482-48	L	S-3	2	61.1
C482-49	L	S-3	1	39.0
C482-50	L	S-3	4	80.8
C482-51	L	S-3	2	61.5
C482-52	L	S-4	2	52.2
C482-53	L	S-4	1	29.5
C482-54	L	S-4	4	71.1
C482-58	L	S-4	2	53.5
C482-61	L	S-4	3	63.9
C482-62	L	S-2	2	43.2
C482-67	C	S-3	2	80.6
C482-68	C	S-3	1	45.8
C482-69	C	S-3	0.5	24.7
C482-70	C	S-3	3	90.5

a. V = Vicron limestone, L = Longview hydrated lime, C = Corson pressure-hydrated lime.

b. B = burner, S-2 = furnace section 2, S-3 = furnace section 3, S-4 = furnace section 4.

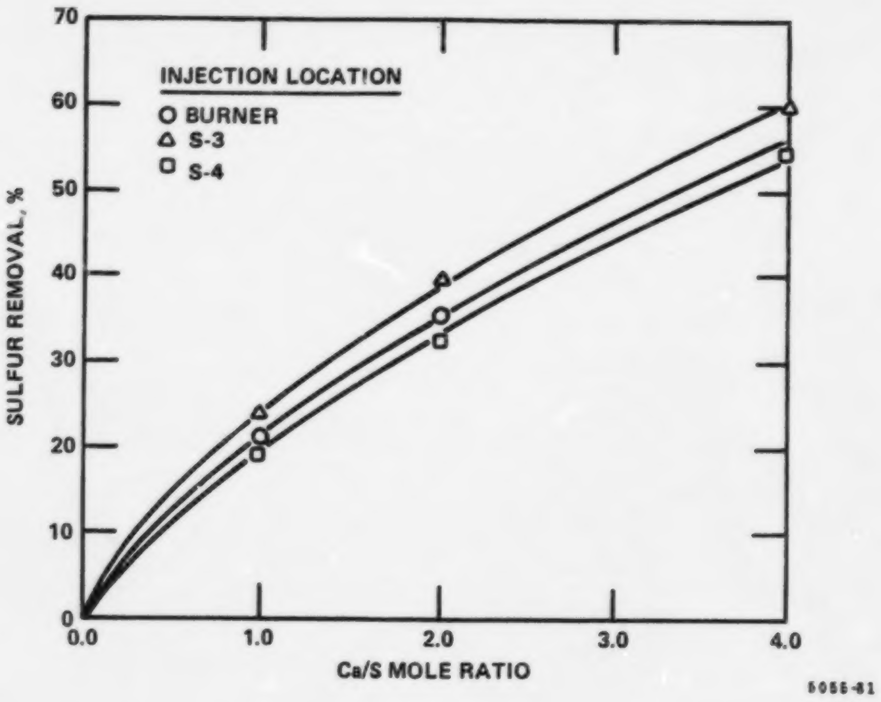

Figure 10. Sulfur capture data obtained with Vicron 45-3 limestone with Indiana Batch No. 3 coal.

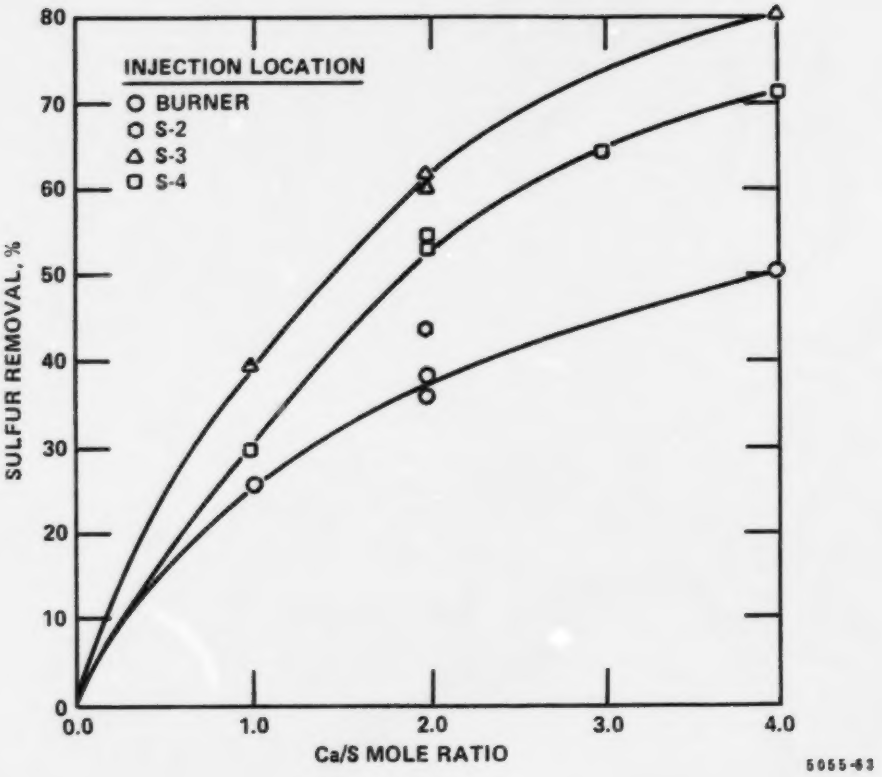

Figure 11. Sulfur capture data obtained with Longview hydrated lime with Indiana Batch No. 3 coal.

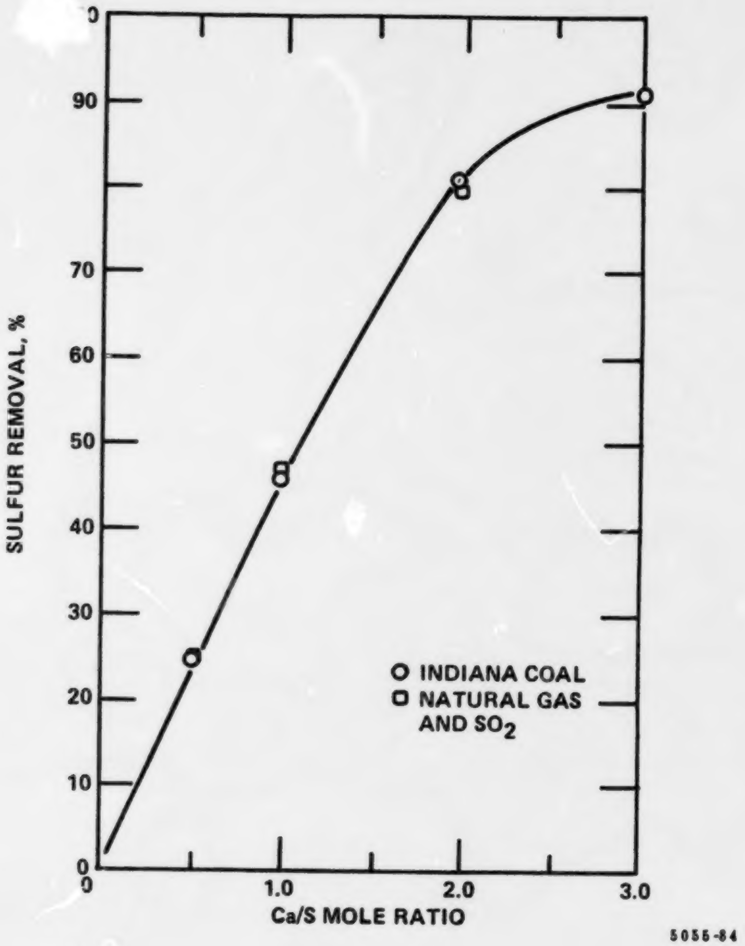

Figure 12. Sulfur capture data obtained with Corson pressure-hydrated, dolomitic lime with Indiana Batch No. 3 coal.

Longview hydrated lime and the Vicron limestone. The performance of the Corson P-H lime is obviously much better than that of Longview hydrated lime or Vicron limestone for a given Ca/S ratio. However, on an equivalent mass basis, the Corson P-H lime is about the same as the Longview hydrated lime, since the Corson P-H lime contains about 40% magnesium as MgO, and the magnesium does not contribute to the sulfation. Data obtained with natural gas firing are also shown in Figure 5 for comparison. The results obtained with coal and natural gas are virtually identical. This is because the maximum gas temperatures are quite similar as shown below:

Furnace location	Maximum gas temperature (°C [°F]) Batch No. 3 coal	Natural gas
S-3	1237 [2260]	1332 [2430]
S-4	1132 [2070]	1126 [2060]
S-5	1048 [1920]	1071 [1960]

These are the maximum temperatures measured during a radial traverse across a given furnace section using the HVT.

Table 8 gives a summary of the sulfur capture data obtained with the three different sorbents with SO_2-doped natural gas. The sorbents tested were: Vicron 45-3 $CaCO_3$, Longview $Ca(OH)_2$, and Corson pressure-hydrated $Ca(OH)_2$-$Mg(OH)_2$. The results obtained with the Corson P-H lime with SO_2-doped natural gas are virtually identical to the results obtained with this sorbent with the Indiana Batch No. 3 coal. For the Longview hydrated lime, however, injection at S-3 with SO_2-doped natural gas gave significantly lower removals than injection at the same location with the coal. This may be attributed to the higher gas temperatures at S-3 with natural gas firing. In the experiments listed in Table 8, the maximum gas temperature at S-3 averaged around 1337°C (2440°F), as opposed to 1238°C (2260°F) with coal firing. Although this may explain the different results obtained with natural gas and coal with the Longview hydrated lime, it cannot explain the similarity in results obtained with natural gas and coal with the Corson P-H lime. Perhaps the Corson P-H lime is less sensitive to an increase in temperature in the range given above.

As was the case with coal firing, the sulfur capture obtained with Vicron 45-3 $CaCO_3$ with gas firing does not appear to be very sensitive to the injection location or the maximum temperature to which it is exposed. This is illustrated in the table below:

Injection location	Maximum temperature (°C [°F])	Sulfur capture (%)
B	1477 [2690]	29-31
S-3	1360 [2480]	22-28
S-4	1171 [2140]	27-30

The sulfur removal obtained with the Longview lime is quite sensitive to the maximum temperature to which the sorbent is exposed in the furnace, as illustrated in Figure 13. Exposure to a maximum gas temperature of about

TABLE 8. SUMMARY OF SULFUR REMOVAL DATA OBTAINED WITH THREE DIFFERENT SORBENTS WITH SO_2-DOPED NATURAL GAS

Run No.	Sorbent[a]	Injection location[b]	Ca/S ratio (mole/mole)	Sulfur capture (%)
C482-74	C	S-3	0.5	25.0
C482-75	C	S-3	1.0	43.9
C482-76	C	S-3	2.0	79.6
C482-83	L	S-3	2.0	45.1
C482-84	L	S-3	1.0	24.8
C482-85	L	S-3	4.0	71.5
C482-87	L	S-3	2.0	52.7
C482-89	L	S-3	1.0	27.5
C482-90	L	S-3	2.0	45.6
C482-91	L	S-4	2.0	51
C482-92	L	B	2.0	32.6
C482-93	L	B	2.0	28.7
C482-118	L	S-4	2.0	44.1
C482-119	L	S-4	2.0	45.1
C482-120	L	S-3	2.0	38.7
C482-121	L	S-3	2.0	40.2
C482-123	L	B	2.0	28.1
C482-124	L	B	2.0	28.7
C482-127	V	B	2	31.0
C482-128	V	B	2	29.4
C482-129	V	S-3	2	27.3
C482-130	V	S-3	2	21.9
C482-131	V	S-3	2	24.9
C482-132	V	S-4	2	29.9
C482-133	V	S-4	2	26.8
C482-137	L	S-3	2.0	39.5
C482-139	L	S-3	2.0	40.5
C482-141	L	S-3	2	48.5[c]
C482-144	L	S-3	2	52.2[c]
C482-146	L	S-3	2	53.5[c]
C482-149	L	S-3	2	53[c]
C482-151	L	S-3	2	56.6[c]
C482-153	L	S-3	2	60.3[c]
C482-154	L	S-3	2	56.3[c]
C482-156	L	S-3	2	46.9[c]
C482-158	L	S-3	2	58.2[c]
C482-160	L	S-3	2	53.4[c]

a. V = Vicron limestone, L = Longview hydrated lime, C = Corson pressure-hydrated lime.

b. B = burner, S-3 = furnace section 3, S-4 = furnace section 4.

c. Reduced load.

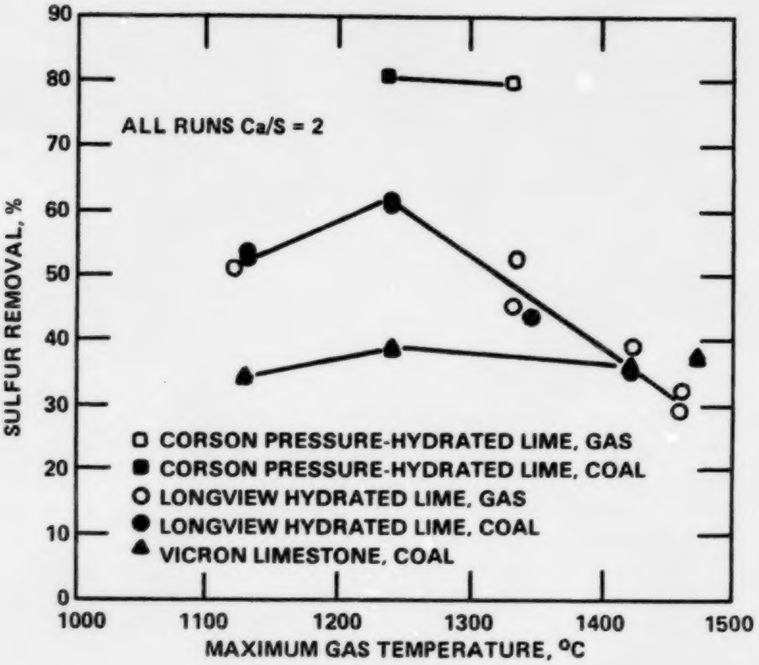

Figure 13. Sulfur capture as a function of the maximum gas temperature to which the sorbent is exposed.

1238°C (2260°F) appears to yield near optimum SO_2 capture with the Longview hydrated lime. Data obtained with Vicron limestone and Corson P-H lime are also shown in Figure 13 for comparison. These data show the relative insensitivity of Vicron limestone to the exposure temperature.

The Corson P-H lime also appears to be relatively insensitive to temperature over the limited range that was investigated with that sorbent. Figure 13 dramatically illustrates the superiority of the Corson P-H lime over the other sorbents when compared on the basis of equal Ca/S ratios. However, it must be noted that the dolomitic P-H lime is only about 55 wt % calcium (as CaO). Therefore, in order to provide the same Ca/S ratio as $CaCO_3$ or $Ca(OH)_2$, it is necessary to inject almost twice as much of the dolomitic material. On an equivalent mass basis, therefore, the Corson P-H lime gives about the same performance as the Longview hydrated lime.

At a Ca/S mole ratio of 2:1, the Marianna limestone and the Pelican hydrated lime gave sulfur captures of 37 and 58% with S-4 injection while firing Hallmark Batch 1 coal. The superior performance of the Marianna limestone over the Vicron may be partially due to the higher initial surface area of the Marianna stone. The Marianna stone also attains a higher area after calcination in the pilot combustor. The performance of the Pelican hydrated lime was essentially the same as the Longview material.

Effect of Furnace Load, Burner Stoichiometry, and Injection Method

In view of the preliminary results indicating generally low SO_2 capture with limestone, it was decided that a series of screening tests should be done to determine whether higher SO_2 captures could be attained under any other set of operating conditions. Table 9 gives the results of the first series of screening tests. In this series of tests, the primary independent variables were the load, or firing rate, the burner stoichiometry (SR_P and SR_B), and the sorbent injection location. Three different loads, four different sorbent injection locations, and a range of burner stoichiometries were investigated as follows:

Load

- normal = 1.06 GJ/hr (1.0 x 10^6 Btu/hr)
- low = 0.78 GJ/hr (0.74 x 10^6 Btu/hr)
- high = 1.38 GJ/hr (1.3 x 10^6 Btu/hr)

Stoichiometries

- primary: $0.10 < SR_P < 0.28$
- burner: $0.57 < SR_B < 1.17$
- overall: $1.10 < SR_O < 1.30$

Sorbent Injection Location

- primary air

TABLE 9. RESULTS OF SCREENING STUDIES OF THE EFFECT OF LOAD, BURNER STOICHIOMETRY, AND SORBENT INJECTION LOCATION ON SO_2 CAPTURE[a]

Doping agent	Load (GJ/hr [10^6 Btu/hr])	SR_P	SR_B	SR_O	Sorbent injection location	Ca/S	SO_2 (ppm)	Capture[b] (%) A	Capture[b] (%) B	Notes
SO_2	1.06 [1.0]	0.27	0.58	1.21	Tertiary air	0	1540	--	--	
						1	1380	7	10.4	
						2	1240	18	19.5	
SO_2	1.06 [1.0]	0.27	0.58	1.21	Primary air	0	1500	--	--	
						1	1250	12	16.7	
						2	980	26	34.7	
SO_2	1.06 [1.0]	0.27	0.58	1.21	Furnace S-4	2	940	--	37.3	
SO_2	0.78 [0.74]	0.28	0.72	1.30	Primary air	0	2080	--	--	
						2	1400	27	32.3	
SO_2	1.38 [1.3]	0.13	0.90	1.10	Primary air	0	1660	--	--	
						1	1320	14	20.5	
SO_2	1.38 [1.3]	0.13	0.57	1.10	Primary air	1	1280	--	22.9	
SO_2	1.38 [1.3]	0.13	0.57	1.10	Furnace S-4	1	1320	--	20.5	
SO_2	1.06 [1.0]	0.16	0.72	1.27	Square duct Sight port	0	1920	--	--	
						1	1600	10	16.7	
						2	1460	--	--	
SO_2	1.06 [1.0]	0.11	1.17	1.17	Primary air	0	2040	--	--	
						1	1740	12	14.7	
						2	1320	27	35.2	
SO_2	1.06 [1.0]	0.10	0.60	1.20	Primary air	2	1320	--	35.2	
H_2S	1.06 [1.0]	0.10	0.60	1.20	Primary air	0	2200	--	--	
						2	1320	--	40.0	
H_2S	1.06 [1.0]	0.17	0.59	1.11	Primary air	0	2160	--	--	70° Swirl
						2	1600	11	25.9	70° Swirl
						2	1540	--	28.7	30° Swirl
						2	1560	--	27.8	10° Swirl
						2	1560	--	27.8	0° Swirl

a. Fuel, natural gas; sorbent, Vicron limestone; distributed mixing burner (DMB) was used except for last screening study, which used an adjustable swirl burner (ASB).

b. Column A shows initial drop from baseline, which was not always reestablished between tests, and hence not given for every condition. Column B shows value calculated from controlled value and last available baseline.

- tertiary air
- S-4 (near furnace outlet)
- square duct sight port, SD-1 (entrance of horizontal duct)

Different calcium-to-sulfur ratios were also studied as indicated in the table. The flue gas temperatures at the latter two sorbent injection locations are typically about 1204 and 1093°C (2200 and 2000°F), respectively.

All of these tests were performed using the distributed mixing burner (DMB). The natural gas was premixed with the primary air, and the dopant (either SO_2 or H_2S) was added just ahead of the burner.

Two of the tests were done using H_2S instead of SO_2 as the dopant, and a comparable change in the SO_2 concentration was noted. One of the tests was done with a different burner having mechanically adjustable swirl vanes. This was done to investigate the effect of independently varying the degree of swirl. It was thought that this would have the effect of varying the degree of mixing between the sorbent and the gas. The swirl angle, or the degree of mixing, apparently had little or no effect on the SO_2 capture since the SO_2 concentration remained relatively constant over the range of 0 to 70° swirl.

The results described above indicated relatively low SO_2 capture in natural gas. These poor results were initially attributed to a lack of residence time in the critical temperature window of 1204 to 871°C (2200 to 1600°F). This may be the case at normal load conditions, but low-load tests, where the residence time in this window was more than doubled, still yielded poor SO_2 capture.

Further Investigations of SO_2 Capture with Sorbent Characterization

Two other test series were performed with SO_2-doped natural gas: one at full load (1.06 GJ/hr or 1.0 x 10^6 Btu/hr) and one at reduced load (0.75 GJ/hr or 0.71 x 10^6 Btu/hr). These tests were primarily intended to generate samples of calcined and sulfated sorbent that could be characterized in the laboratory in order to determine whether the poor SO_2 capture could be due to insufficient calcination or inadequate surface area in the sorbent.

The conditions for the full-load test series are given in Table 10, which is actually a compilation of the sampling conditions for the sorbent samples that were collected. The samples were collected in mass train thimbles at a temperature of 171 to 182°C (340 to 360°F). Samples were collected with and without SO_2 in the system as indicated in the table. All of the samples were generated at full load with the combustor coaxially staged using four 5.08-cm (2-in.) tertiary ports. The burner stoichiometries were maintained as constant as possible at the following values: $SR_P = 0.08$, $SR_B = 0.60\text{-}0.69$, and $SR_O = 1.14\text{-}1.21$.

The first two samples were generated using a burner configuration intended to simulate that used by the Energy and Environmental Research Corporation (EERC). In this configuration, the natural gas was injected axially through a

TABLE 10. SAMPLING CONDITIONS FOR CALCINED AND SULFATED SORBENTS GENERATED IN NATURAL GAS AT FULL LOAD[a]

Sample I.D. No.	Secondary air temp (°C [°F])	SR_P[b] (%)	SR_B (%)	SR_O (%)	Doping agent	O_2 (%)	CO_2 (%)	NO_x (ppm)	SO_2 (ppm)	Sample temp (°C [°F])	H_2O (%)	Sample weight (mg)	Loading (mg/scm)
MT-1[c]	67 [153]	8	69	121	None	2.9	10.1	40	0	182 [360]	18.3	2950	5050
MT-2[c]	67 [153]	8	69	121	SO_2	3.5	9.5	35	1080	182 [360]	16.9	7370	12740
MT-3[d]	278 [533]	8	62	118	SO_2	3.0	10.0	30	1480	171 [340]	20.4	1630	3110
MT-4[d]	278 [533]	8	62	118	SO_2	3.2	10.0	30	1380	171 [340]	18.3	2210	2880
MT-5[d]	278 [533]	8	62	118	SO_2	2.7	10.5	30	1140	171 [340]	19.1	2440	3220
MT-6[d]	287 [548]	8	60	114	None	2.6	10.4	30	0	171 [340]	20.1	2110	2790
MT-7[d]	287 [548]	8	60	114	None	2.5	10.4	30	0	171 [340]	19.3	2280	3015
MT-8[d]	287 [548]	8	60	114	None	2.5	10.3	30	0	171 [340]	20.0	2260	2990

a. All samples generated in SRI combustor while firing natural gas at full load (1.06 GJ/hr or 10^6 Btu/hr). Vicron limestone added to primary airstream. Staging is axial using four 5.0-cm (2-in.) tertiary air ports.

b. Primary stoichiometric ratio includes estimated quantity of air drawn in by the sorbent aspirator.

c. Burner arrangement similar to that used at EERC. Natural gas is injected through a 1.9-cm (0.75-in.) pipe along the centerline. Primary air and sorbent are introduced through an annulus surrounding the gas injector. No air preheat is used.

d. Normal SRI distributed mixing burner configuration. Natural gas, primary air, and sorbent are premixed ahead of burner.

1.9-cm (0.75-in.) pipe along the furnace centerline. The primary air and sorbent were introduced through a surrounding annulus. No air preheat was used in this mode of operation. This produced a long, lazy flame that was generally much cooler than the gas flames produced with the normal DMB configuration. In the EER-type configuration, two samples were obtained: one with SO_2 added to the gas, and one without SO_2 addition.

The remaining samples were produced using the normal DMB configuration with the natural gas, primary air, and sorbent premixed ahead of the burner. In this operating mode, the secondary and tertiary airstreams were preheated as indicated in the table. Three samples were obtained with SO_2 added to the gas, and three samples were obtained without SO_2 addition.

Sample MT-2 may contain material that was reentrained from the system walls; at least, that appears to be the most likely explanation for the disproportionately high mass loading, although there was no evidence of this in the chemical analysis of the sample. There were no obvious problems with the other samples.

Based on analyses of the samples, it appears that the sorbent utilization was about 6.5% for MT-2 and about 11% for MT-3, -4, and -5. The complete sample analyses are given in Table 11. The low values of LOI suggest that all of the samples were thoroughly calcined. These results indicate that the generally poor SO_2 capture obtained with limestone in these tests cannot be attributed to a lack of calcination.

The last experiments in this series with doped natural gas were performed at low load (0.75 GJ/hr or 0.71 x 10^6 Btu/hr) where the time-temperature profile was thought to be more favorable to SO_2 capture. In these tests, the Vicron limestone was again added to the primary air which was premixed with the natural gas and doped with SO_2 just ahead of the burner. The staging was again coaxial using four 5.0-cm (2-in.) tertiary air ports in the standard DMB configuration. The load, the burner stoichiometries, and the sorbent injection rate were all maintained constant at the values given below:

- Load = 0.75 GJ/hr (0.71 x 10^6 Btu/hr)
- SR_P = 27%
- SR_B = 78%
- SR_O = 125%

- Sorbent injection rate = 7.08 kg/hr (15.6 lb/hr)

The estimated gas-phase SO_2 captures obtained under these conditions are summarized below:

Ca/S	Gas-phase SO_2 capture (%)
1	10-11
2	20-22
4	33-44

TABLE 11. ANALYSES OF CALCINED AND SULFATED SORBENT SAMPLES

Sample I.D. No.	% LOI[a]	% Ca^{+2}	% SO_4^{-2}	S/Ca	BET (m^2/g)
MT-1	4.2	69.6	--	--	4.19
MT-2	1.7	64.6	10.0	6.5	3.04
MT-3	1.0	60.8	16.2	11.1	3.36
MT-4	1.9	63.2	16.7	11.0	3.58
MT-5	0.7	61.9	16.9	11.4	3.16
MT-6	1.9	68.8	--	--	4.13
MT-7	2.5	68.4	--	--	4.04
MT-8	3.8	69.2	--	--	4.17
132-86-3	5.5	57.7	--	--	NA[b]
132-86-4	2.8	63.7	--	--	NA[b]

[a] Percent weight loss on ignition at 750°C (1382°F).

[b] Not available.

Under the above conditions, one sorbent sample was collected with SO_2 in the system, and five samples were collected without SO_2. The sampling conditions are detailed in Table 12. The baseline SO_2 value given in the table is the SO_2 concentration measured before sorbent injection, so it is not corrected for wall removal. During the collection of the sulfated sorbent sample, the SO_2 concentration was steadily decreasing from 1160 to 960 ppm, presumably due to wall removal. There was no SO_2 in the system while the other (calcined) samples were collected. The five samples of calcined sorbent collected without SO_2 in the system included three samples collected in mass train thimbles at 87.8 to 110°C (190 to 230°F) and two samples collected at much higher temperatures in a particle-quench probe (PQP). The PQP uses a 5:1 dilution of the flue gas sample with nitrogen gas in order to quench the reaction of the CaO with the SO_2. The PQP is also water cooled, so that it can be used in the furnace itself. The mass loading cannot be accurately determined with the PQP, however, due to loss of sample in the probe ahead of the filter, and because it does not provide an isokinetic sample. The PQP was used to collect sorbent samples at two locations: one in the flame zone of the furnace where the flue gas temperature was about 1204 to 1260°C (2200 to 2300°F), and one near the outlet of the furnace where the flue gas temperature was about 871 to 927°C (1600 to 1700°F). The higher temperature sample lost only 5.5% of its weight when held at 750°C (1382°F) for 2 hr. This indicates that the sorbent is thoroughly calcined before reaching a temperature of 1204 to 1260°C (2200 to 2300°F) (i.e., before entering the critical temperature window of 1204 to 871°C or 2200 to 1600°F). The sample collected at 871 to 917°C (1600 to 1700°F) had a loss on ignition of only 2.8%. These results strongly suggest that the poor SO_2 capture cannot be attributed to a lack of calcination.

Analysis of SO_2 Capture in Terms of the Time-Temperature Profile

Figure 14 shows gas temperature profiles based on HVT and thermocouple measurements made at full load (1.06 GJ/hr or 1.0 x 10^6 Btu/hr) and reduced load (0.795 GJ/hr or 0.75 x 10^6 Btu/hr). These measurements were made during staged (SR_B ~0.6) combustion of natural gas. The time-temperature profiles were calculated from the actual temperature measurements assuming plug flow through the system. The temperatures in the furnace and square duct were measured along the centerline using the HVT; the downstream temperatures were measured by thermocouples. These pyrometer measurements were made without sorbent added to the primary air, but with the same amount of primary air, including the sorbent transport air. The location of the sampling point for the continuous gas analyzers is indicated by an asterisk on each time-temperature profile.

Some important features of the two time-temperature profiles are summarized below:

Load, GJ/hr (Btu/hr)	1.06 (1 x 10^6)	0.795 (0.75 x 10^6)
Peak flame temperature, °C (°F)	1510 (2750)	1315 (2400)
Residence time between 1204 and 871°C (2200 and 1600°F), sec	1.1	2.7

TABLE 12. SAMPLING CONDITIONS FOR CALCINED AND SULFATED SORBENT GENERATED IN NATURAL GAS AT LOW LOAD[a]

SR_P = 27% O_2 = 3.5% Load = 0.75 GJ/hr (0.7 x 10^6 Btu/hr)

SR_B = 78% CO_2 = 9.2% Sorbent rate = 7.08 kg/hr (15.6 lb/hr)

SR_O = 125% NO_x = 10 to 20 ppm H_2O = 17.2%

Sample I.D No.	Doping agent	SO_2 (ppm)	SO_2 baseline[b]	Sample temp (°C [°F])	wt (mg)	(mg/scm [gr/dscf]
132-69-1	SO_2	1160-960	1800	87.8 [190]	5440	7,585 [3.31]
132-78-1	None	0	--	104 [220]	3630	5,015 [2.19]
132-78-2	None	0	--	103 [218]	6760	9,580 [4.18]
132-86-2	None	0	--	110 [230]	7580	10,400 [4.54]
132-86-3[c]	None	0	--	1204-1260 [2200-2300]	5810	--[d]
132-86-4[c]	None	0	--	871-927 [1600-1700]	5790	--[d]

a. Vicron limestone added to primary airstream. Staging is axial using four 5.0-cm (2-in.) tertiary air ports with standard DMB configuration.

b. SO_2 concentration before sorbent addition; not corrected for wall removal.

c. Sample collected in particle quench probe (PQP).

d. Loading cannot be accurately determined with PQP due to nonisokinetic sampling and loss of material in probe ahead of filter.

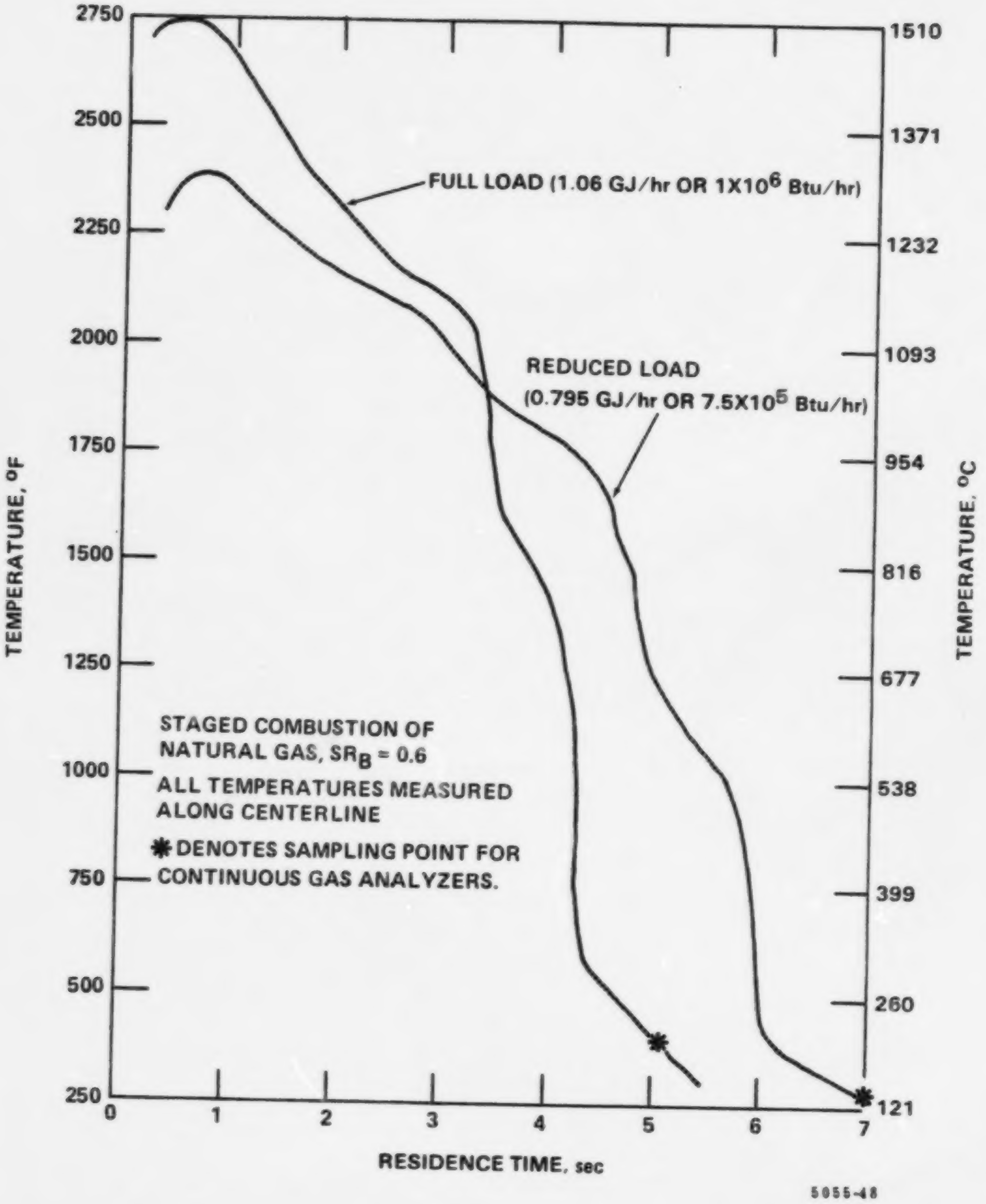

Figure 14. Temperature profiles measured with natural gas firing at full load and 75% load.

A comparison of the two profiles shows that the reduced-load profile has a lower peak flame temperature, along with over twice as much residence time in the critical temperature window. These factors should favor SO_2 removal at reduced load, but the SO_2 capture data show only a slight improvement at reduced load, as indicated in Table 13. Data obtained with an Illinois coal are also shown for comparison. If only the short-term results are considered, the SO_2 removals at Ca/S = 2 may be compared as follows:

- Natural gas, reduced load: capture = 20 to 22%
- Natural gas, full load: capture = 15%
- Illinois coal, full load: capture = 21 to 28%

Although the Illinois coal appears to give better SO_2 capture, it should be noted that it produced a significantly higher SO_2 concentration, and the SO_2 capture is dependent upon the initial concentration of SO_2 present.

From the results discussed above, it appears unlikely that the time-temperature profile can provide the entire explanation for the poor SO_2 capture. Furthermore, the analytical results show that a lack of calcination is not the problem. The low capture at full load may be attributed to inadequate residence time in the temperature window. At low load, however, this residence time is more than doubled.

Three possible explanations for the relatively poor SO_2 capture obtained in these tests with natural gas are: (1) inadequate mixing between the sorbent and flue gas, (2) a difference in particle residence time distributions, or (3) differences in the surface properties and/or activities of the calcines produced in the respective furnaces. The experimental results obtained with different degrees of swirl seem to argue against inadequate mixing as the explanation. Visual observations of the sorbent mixing patterns have been made, but different observers have expressed differing opinions concerning the quality of the mixing. The question concerning possible differences in particle residence times is not easily answered. It may be possible to estimate particle residence times by using sorbent particles that are labeled with tracers. The residence times could be estimated from the time intervals between the introduction of the labeled material into the system and its detection at various points downstream.

Chemical Composition and Sorbent Utilization in Size-Fractionated Ash/Sorbent Mixtures

In order to determine how sorbent utilization varies with particle size in ash/sorbent mixtures, size-fractionated samples of ash and ash/sorbent mixtures have been analyzed. Analyses were done on four sets of five-stage cyclone samples and two sets of Bahco samples, which were produced under the following conditions:

(1) Baseline - Indiana Batch No. 2 coal - no sorbent - five-stage cyclone sample + Bahco sample;

TABLE 13. GAS-PHASE SO_2 CAPTURES MEASURED AT REDUCED LOAD AND FULL LOAD

Fuel	Load (GJ/hr [10^6 Btu/hr])	Baseline SO_2 ppm at 3% O_2	Ca/S	% Removal (at stated time [min])
Natural gas	0.742 [0.7]	2000	1	9.7 [5]
			2	20 [5]
			4	33 [5]
Natural gas	0.742 [0.7]	1900	1	11 [4]
				14 [13]
			2	22 [8]
			4	33 [4]
				44 [25]
Natural gas	1.06 [1.0]	1650	1	11 [3]
				12 [5]
			2	15 [4]
				15 [6]
			4	20 [4]
				20 [6]
Illinois coal	1.06 [1.0]	2800	1	14 [2]
				19 [5]
			2	21 [3]
				28 [4]
				34 [8]
			4	29 [5]
				50 [10]

All tests: - Vicron limestone with fuel.
- DMB (axial staging).
- SR_P ~0.3, SR_B = 0.7 to 0.8.

(2) Vicron limestone at burner - Vicron 45-3 limestone added at the burner at a rate of 4.63 kg/hr (10.19 lb/hr) (Ca/S ~1.9) - five-stage cyclone sample only;

(3) Vicron limestone at S-4 - Vicron limestone added at the same rate at S-4 - five-stage cyclone sample only;

(4) Longview hydrated lime at S-4 - Longview hydrated lime added at S-4 at rate of 3.42 kg/hr (7.54 lb/hr) (Ca/S ~1.9) - five-stage cyclone + Bahco sample.

All of the above samples were obtained while firing the Indiana Batch No. 2 coal at a rate of about 36.3 kg/hr (80 lb/hr), corresponding to a thermal input of about 1.06 GJ/hr (1 x 10^6 Btu/hr). Based on the average coal sulfur content of 2.16%, the injection rates corresponded to a Ca/S mole ratio of 1.9:1. The combustor was coaxially staged during all of this work. The burner and tertiary air rates represented 76 and 48% of the stoichiometric air requirement when the sorbent and sorbent transport air were added at the burner. When the sorbent and sorbent transport air were added at S-4, the burner air represented only 66% of the stoichiometric air but the overall stoichiometric ratio was held constant at 124%.

With the Vicron limestone added at the burner and at S-4, the SO_2 removals after 10 min were about 35 and 40%, respectively. With Longview hydrated lime added at S-4, the SO_2 removal after 10 min was about 45%. The run data for the five-stage cyclone runs are given in Table 14.

Figure 15 is a plot of Fe_2O_3, Al_2O_3, and SiO_2 as a function of particle size in the fly ash from the Indiana No. 2 coal. The plot is based on both five-stage cyclone data covering the range of about 0.2 to 5 µm and Bahco data covering the range of about 1.3 to 32 µm. The cyclone and Bahco data agree very well for Fe_2O_3, but not for SiO_2 and Al_2O_3. Nevertheless, both sets of data show definite trends with decreasing particle size: Fe_2O_3 increases, SiO_2 decreases, and Al_2O_3 remains about the same. Apparently, the increase in Fe_2O_3 is offset by a decrease in SiO_2.

Figure 16 is a plot of Fe_2O_3, Al_2O_3, SiO_2, CaO, and SO_3 as a function of particle size in an ash/sorbent mixture produced by addition of Vicron limestone at the burner during combustion of the Indiana Batch No. 2 coal. In addition to the same trends shown in Figure 15, Figure 16 also shows increasing SO_3 and decreasing CaO as the particle size decreases. This suggests that the fraction of fly ash in the ash/sorbent mixture increases with decreasing particle size as well.

Figure 17 shows the same thing given in Figure 16, except that, in this case, the Vicron limestone was added at S-4 instead of at the burner. It is instructive to compare the trends in SO_3 and CaO to those illustrated in Figure 17. Note that the degree of variation with particle size is not as great with injection at S-4, as it is with injection at the burner. In other words, it appears that the sorbent utilization is less sensitive to particle size with

TABLE 14. CYCLONE RUN DATA

Cyclone Run No. CYC-NOC-0280-113
(Indiana coal, no sorbent)
Sampling rate = 14.1 L/min (0.500 scfm) Temperature = 154°C (310°F)

Stage No.	Cut point (μm)	Mass collected (mg)
1	5.18	2000.8
2	2.05	306.4
3	1.30	232.7
4	0.57	237.9
5	0.25	25.7
F	--	39.0

Cyclone No. CYC-NOC-0280-116
(Indiana coal + Vicron limestone at burner)
Sampling rate = 15.0 L/min (0.530 scfm) Temperature = 149°C (300°F)

Stage No.	Cut point (μm)	Mass collected (mg)
1	4.65	6175.3
2	1.82	841.2
3	1.14	539.5
4	0.49	509.8
5	0.20	41.3
F	--	24.5

Cyclone Run No. CYC-NOC-0280-118
(Indiana coal + Vicron limestone at S-4)
Sampling rate = 14.9 L/min (0.526 scfm) Temperature = 149°C (300°F)

Stage No.	Cut point (μm)	Mass collected (mg)
1	4.70	6978.5
2	1.84	804.4
3	1.15	456.3
4	0.50	382.0
5	0.20	88.3
F	--	30.9

Cyclone Run No. CYC-NOC-0280-121
(Indiana coal + Longview hydrated lime at S-4)
Sampling rate = 14.2 L/min (0.501 scfm) Temperature = 138°C (280°F)

Stage No.	Cut point (μm)	Mass collected (mg)
1	4.70	3353.4
2	1.86	824.3
3	1.17	897.0
4	0.52	709.3
5	0.22	168.5
F	--	29.3

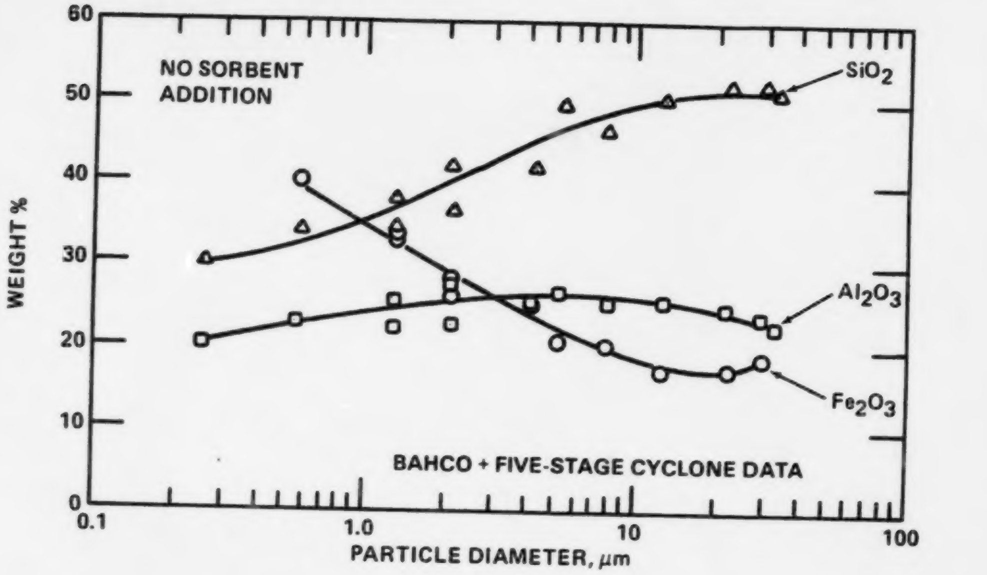

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Figure 15. Size dependence of elemental concentrations in fly ash from Indiana Lot No. 2 coal.

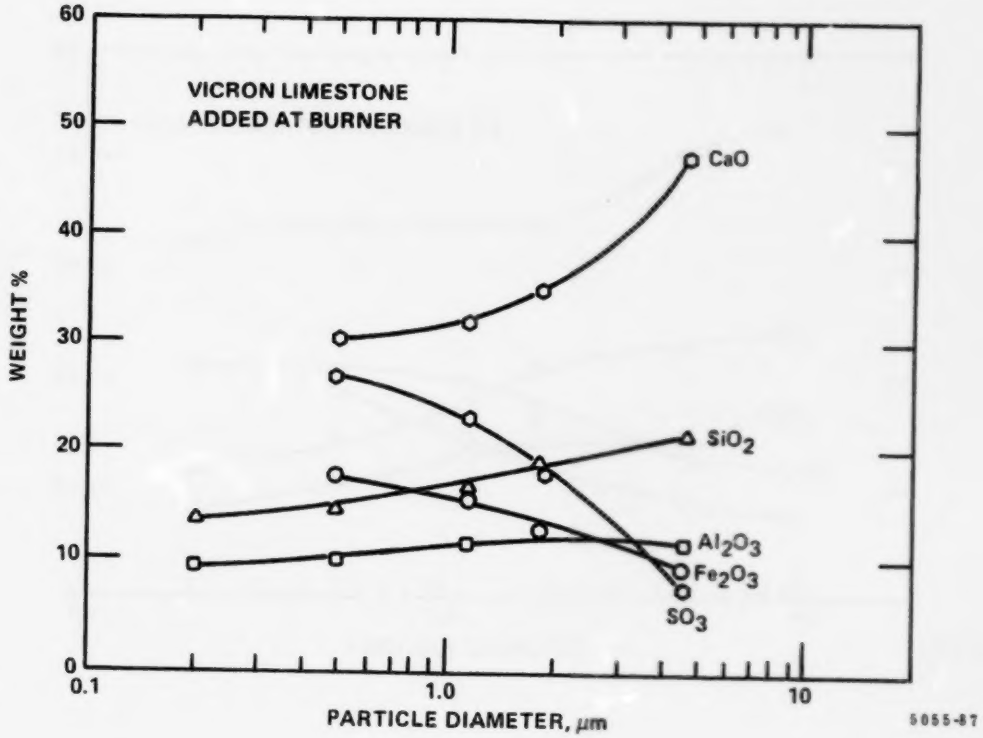


Figure 16. Size dependence of elemental concentrations in an ash/sorbent mixture produced by addition of Vicron limestone at the burner during combustion of Indiana Lot No. 2 coal.

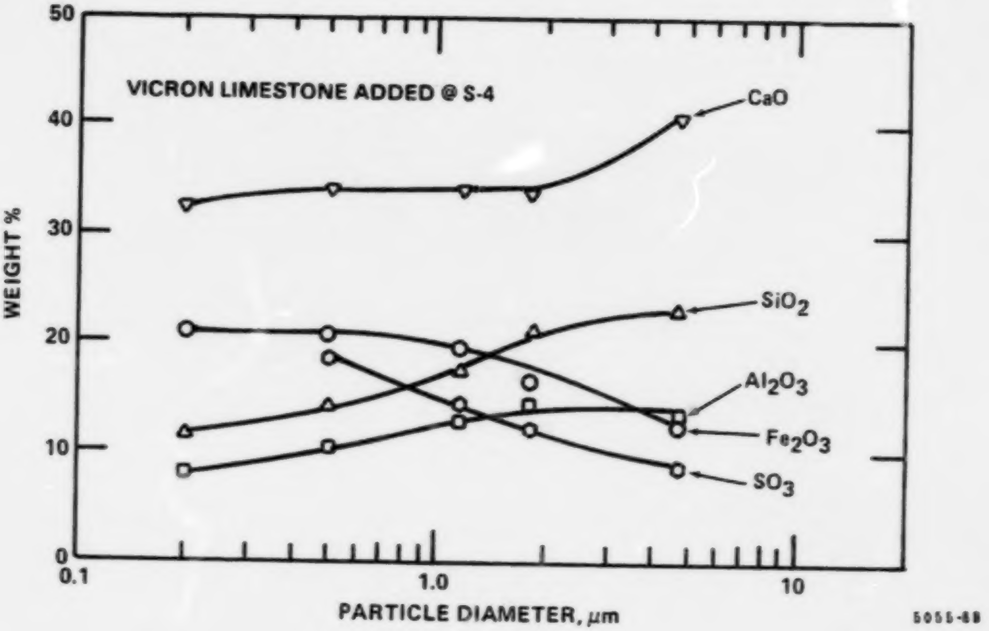


Figure 17. Size dependence of elemental concentrations in an ash/sorbent mixture produced by addition of Vicron limestone at S-4 during combustion of Indiana Lot No. 2 coal.

injection at S-4 than it is at the burner. This might mean that the internal surface is more important at S-4, or conversely that the external surface is more important at the burner. In other words, the internal surface may not be available or it may be unutilized when the sorbent is injected at the burner.

Figure 18 shows a plot of Fe_2O_3, Al_2O_3, SiO_2, CaO, and SO_3 as a function of particle size in an ash/sorbent mixture produced by addition of Longview hydrated lime at S-4 while firing the Indiana No. 2 coal. The trends here are different than those shown in Figures 16 and 17. The most noteworthy difference is the sharp increase in CaO with decreasing particle size over the range of 10 to 0.5 µm. This suggests that the fraction of sorbent in the ash/sorbent mixture increases sharply with decreasing particle size. Recall that the opposite trend was observed with the Vicron limestone. The lack of agreement between the five-stage cyclone results and the Bahco results makes a quantitative analysis difficult, but it appears that the sorbent fraction increases from about 12 to 24% at 10 µm to about 69 to 82% at 0.5 µm. The numerical result depends on which species is used to calculate the fractions of ash and sorbent in the mixture. This is illustrated in Table 15, which shows the calculated percent ash in the mixture based on Fe_2O_3, Al_2O_3, and SiO_2.

Figure 19 is a plot of the calculated weight percent fly ash as a function of particle size in the ash/sorbent mixture produced with the Longview hydrated lime added at S-4. This dramatically illustrates the discrepancy between the cyclone data and the Bahco data in this case (this is unusually poor agreement). It also shows the sensitivity of the results to the choice of Fe_2O_3, Al_2O_3, or SiO_2 as the basis for calculating the mass balance. Nevertheless, both sets of data show a definite trend toward less ash, or more sorbent, in the finer size fractions. The opposite trend was found with the Vicron, suggesting that the Longview hydrated lime is either finer than the Vicron limestone to begin with (as is known to be the case), and/or it decrepitates to a greater extent than the Vicron limestone.

Figures 20 and 21 show the calculated sorbent utilizations as a function of particle size, based on the foregoing results. Surprisingly, the Vicron limestone utilizations are lower at S-4 than at the burner for particle sizes below about 5 µm. There appears to be a crossover around 5 µm, and S-4 appears to give higher utilizations in the larger particles. The match up between the cyclone and Bahco data that appeared to be quite bad in Figure 19 does not appear so bad in Figure 21. It appears that the errors are partially compensating in the utilization calculation, or that the utilization is not that sensitive to the exact fraction of ash and sorbent in the mixture.

The unusually high values of calcium utilization indicated in Figure 21 for submicron particles may be the result of sampling artifacts. It is possible that SO_2 or SO_3 reacted during sampling with the deposits of the unreacted calcine in the cyclone cup. This hypothesis does not explain, however, the apparently higher values of calcium utilization for submicron particles with burner injection compared with S-4 injection.

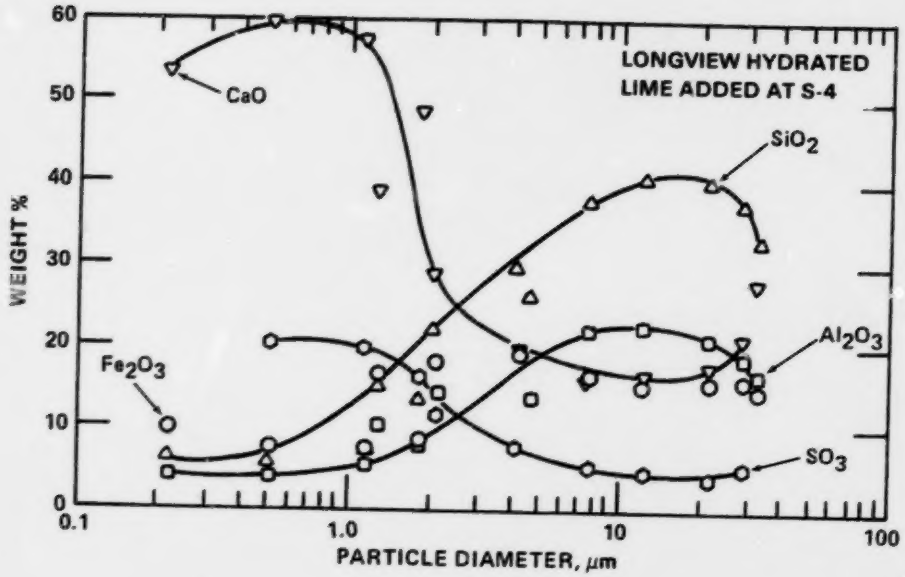


Figure 18. Size dependence of elemental concentrations in an ash/sorbent mixture produced by addition of Longview hydrated lime at S-4 during combustion of Indiana Lot No. 2 coal.

TABLE 15. CALCULATED PERCENT ASH IN MIXTURE BASED ON Fe_2O_3, Al_2O_3, AND SiO_2

Sorbent: Longview hydrated lime   Injection location: S-4

	% i in mixture			% i in ash			% ash in mixture		
D_p (μm)	Fe_2O_3	Al_2O_3	SiO_2	Fe_2O_3	Al_2O_3	SiO_2	Fe_2O_3	Al_2O_3	SiO_2
0.25 (0.22)	9.8	4.0	6.3	--	20.2	30.1	--	19.8	20.9
0.57 (0.52)	7.6	4.0	5.9	40.0	23.1	34.1	19.0	17.3	17.3
1.3 (1.17)	7.6	5.4	7.8	32.8	25.5	38.1	23.2	21.2	20.5
1.3	16.7	10.3	15.1	33.5	22.3	34.5	49.9	46.2	43.8
2.0 (1.9)	8.9	8.3	13.4	26.4	27.2	42.0	33.7	30.5	31.9
2.1	18.1	14.9	22.3	27.9	22.7	36.3	64.9	65.6	61.4
4.2	19.0	19.6	30.0	25.0	25.2	41.6	76.0	77.8	72.1
5.2 (4.7)	11.6	13.7	26.5	20.5	26.6	49.0	56.6	51.5	54.1
7.8	16.7	21.9	37.4	20.1	25.6	46.4	83.1	85.5	80.6
12.4	15.0	22.2	40.2	17.0	25.3	50.1	88.2	87.7	80.2
21.8	15.4	20.7	40.0	17.4	24.7	52.0	88.5	83.8	76.9
29.0	15.7	18.2	37.6	18.6	23.5	52.0	84.4	77.4	72.3
32.5	14.5	16.2	32.8	--	22.5	51.6	--	72.0	63.6

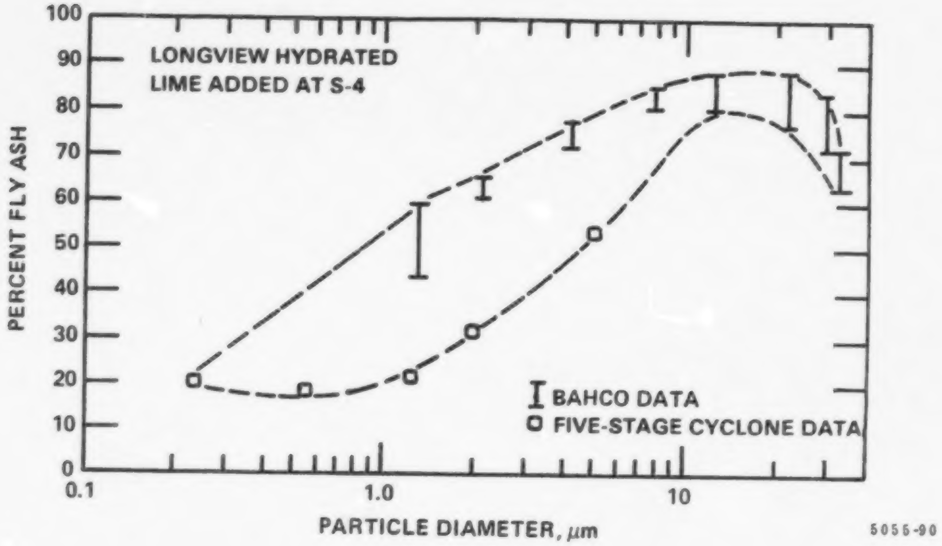


Figure 19. Size dependence of fly ash fraction in ash/sorbent mixture produced by addition of Longview hydrated lime at S-4 during combustion of Indiana Lot No. 2 coal.

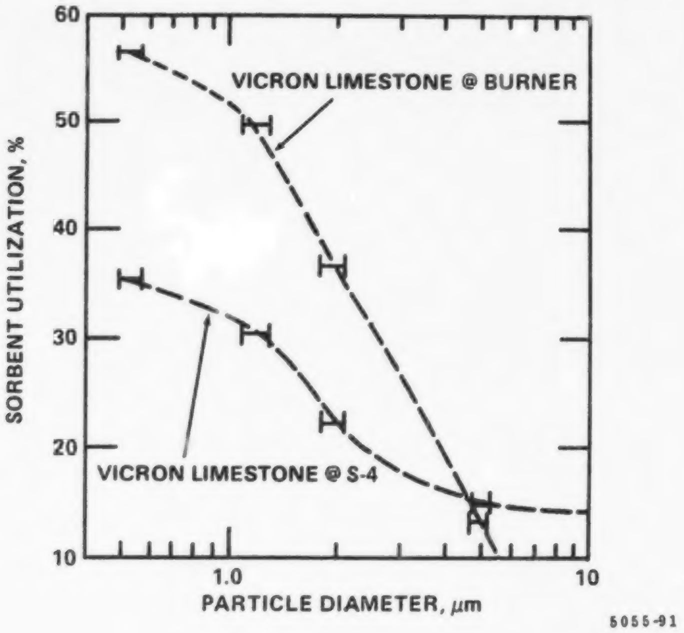


Figure 20. Apparent sorbent utilization as a function of particle size in ash/sorbent mixtures produced by addition of Vicron limestone at the burner and at S-4 during combustion of Indiana Lot No. 2 coal.

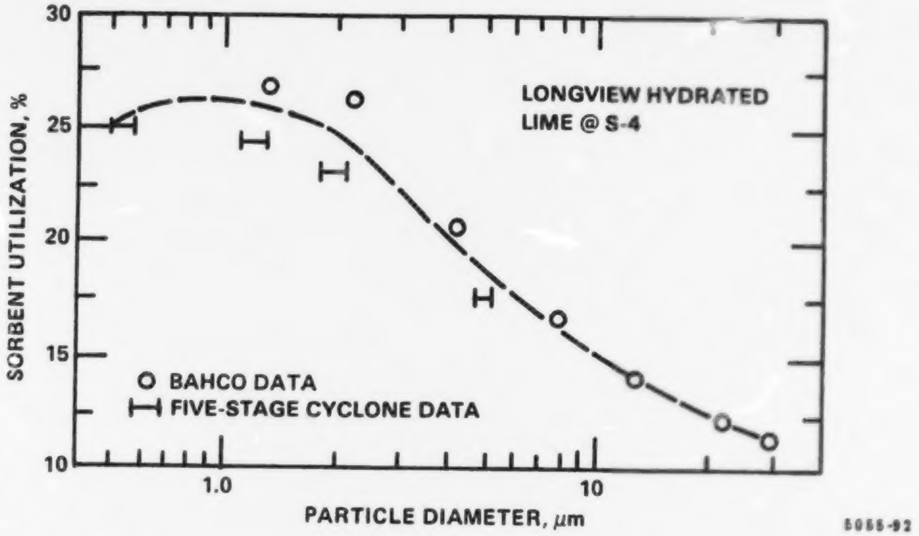


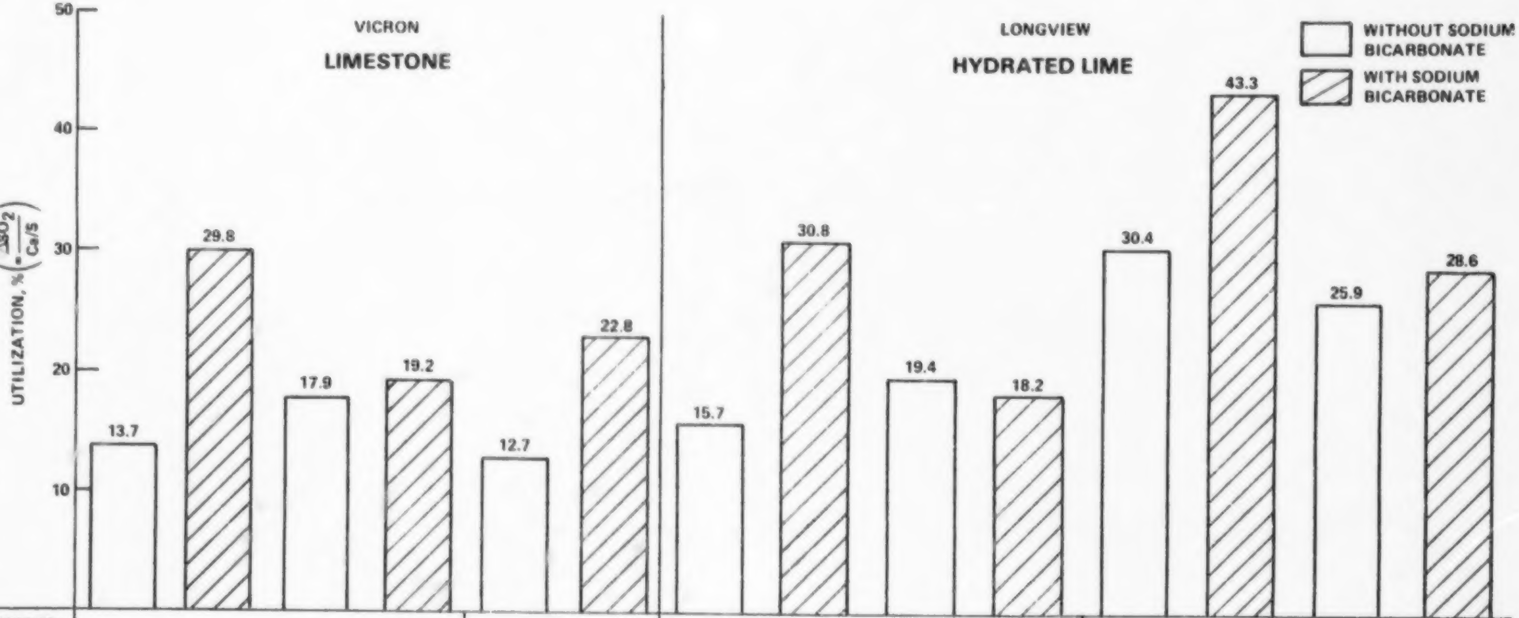
Figure 21. Apparent sorbent utilization as a function of particle size in ash/sorbent mixtures produced by addition of Longview hydrated lime at S-4 during combustion of Indiana Lot No. 2 coal.

Preliminary Evaluations of Additives for Enhanced Sorbent Performance

Preliminary tests were performed to determine the effect of adding sodium bicarbonate and lithium carbonate promoters to Vicron limestone and Longview hydrated lime. During these tests the furnace was operated at 1.06 GJ/hr (1×10^6 Btu/hr) on natural gas or Hallmark coal, no staging, and 30° swirl. Sorbent/sodium bicarbonate mixtures consisted of 95 wt % Vicron limestone and 5 wt % $NaHCO_3$ or 93.4 wt % Longview hydrated lime and 6.6 wt % $NaHCO_3$ (Ca/Na mole ratio = 16) and were mixed by tumbling a 18.9-L (5-gal.) bucket in a cement mixer for 10 to 20 min. The results of these tests are shown in Figures 22 and 23.

With SO_2-doped natural gas, sodium bicarbonate doubled the utilization of either sorbent injected at the burner. Injection of sodium bicarbonate and sorbent at S-4 gave a factor of 1.5 improvement in utilization of either sorbent with gas firing. Thus, with natural gas as the fuel, the sodium bicarbonate promoter was more effective at the burner than at S-4 for both Vicron and Longview sorbents. The sodium-doped sorbents were tested with Hallmark coal, for which no tests have been done with untreated sorbents. However, comparison with either the gas-firing tests or with previous tests using Indiana coal shows that the effectiveness of the sodium as a promoter is greatly reduced for burner injection with coal firing. The promoter also gave little or no enhancement for Longview hydrated lime injected at S-4 during coal firing. This may be explained in terms of the volatilization and condensation of the $NaHCO_3$ promoter. The fly ash particles that are present in the case of coal firing compete with the sorbent particles as sites for condensation of the volatilized sodium species. Consequently, there is less sodium available to the sorbent when coal is fired. This explanation is supported by analyses of sorbent particles collected during natural gas and coal firing. Analyses obtained by secondary ion mass spectrometry (SIMS) show that there is less sodium on the surface of the sorbent particles in the sample with coal firing. The SIMS analyses also show that most of the sodium occurs within the top 500 Å of the sorbent particles. This is consistent with a volatilization-condensation mechanism. This also suggests that a nonvolatile promoter may offer some advantages over a volatile one if it can be dispersed throughout the sorbent by some other mechanism.

Recent work by Borgwardt (11) suggests that lithium may promote sulfur capture at relatively low temperatures (800°C or 1472°F). Lithium carbonate was examined as a possible promoter by injecting a mixture of 94 wt % Vicron limestone, 5 wt % $NaHCO_3$, and 1 wt % Li_2CO_3 into the furnace. The results in Figure 18 show that the addition of 1 wt % Li_2CO_3 at the burner and at S-4 gave improvement factors of 1.11 and 1.05, respectively, over sodium bicarbonate alone. Kaolin was then added to the primary air/natural gas stream at a rate equivalent to a typical ash burden from coal. The reduction in the effectiveness of the combined promoter with burner injection was similar to that observed with coal firing with burner injection of the sodium-doped Vicron limestone. However, the Kaolin had no effect on the enhanced utilization of the Vicron limestone mixture injected at S-4. This contrasts with the results for sodium-doped Longview hydrated lime where the promoter effect was absent with coal firing.



INJECTION LOCATION	BURNER				S-4		BURNER				S-4			
FUEL	NATURAL GAS		INDIANA 3	HALLMARK	NATURAL GAS		NATURAL GAS		INDIANA 3	HALLMARK	NATURAL GAS		INDIANA 3	HALLMARK
SORBENT AND ADDITIVE	100% $CaCO_3$	95% $CaCO_3$ 5% $NaHCO_3$	100% $CaCO_3$	95% $CaCO_3$ 5% $NaHCO_3$	100% $CaCO_3$	95% $CaCO_3$ 5% $NaHCO_3$	100% $Ca(OH)_2$	93.4% $Ca(OH)_2$ 6.6% $NaHCO_3$	100% $Ca(OH)_2$	93.4% $Ca(OH)_2$ 6.6% $NaHCO_3$	100% $Ca(OH)_2$	93.4% $Ca(OH)_2$ 6.6% $NaHCO_3$	100% $Ca(OH)_2$	93.4% $Ca(OH)_2$ 6.6% $NaHCO_3$
Ca/S RATIO	1.7	1.7	2.0	1.7	2.2	1.6	1.5	1.4	1.9	2.0	1.5	1.2	2.0	2.0
BASELINE SO_2	2736	2641	2479	2396	2364	2706	2760	2721	2549	2554	2814	2699	2388	2518
REFERENCE	751-73, -76	C751-82, -85 -124	C482-20, -35	C751-129, -132	C482-132, -133	C751-94, -95	C751-99, -100	C751-101, -102	C482-43, -47	C751-140, -141	C751-97, -98	C751-103, -104	C4[illegible]52, -58	C751-142, -143

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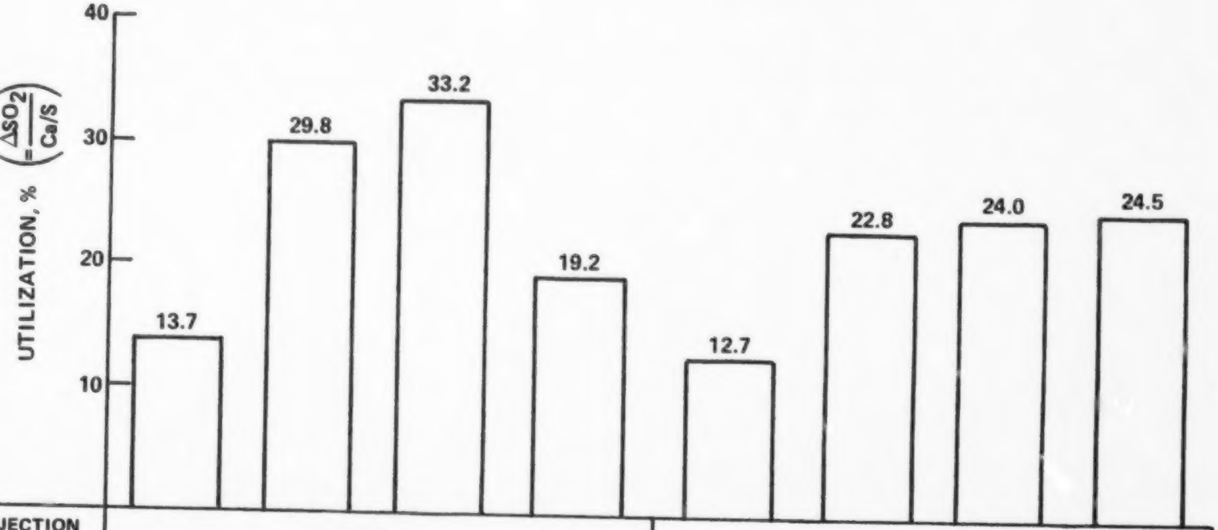
Figure 22. Comparison of Vicron limestone and Longview hydrated lime with sodium bicarbonate promoter at various conditions.



INJECTION LOCATION	BURNER				S-4			
FUEL	NATURAL GAS			NATURAL GAS AND KAOLIN	NATURAL GAS			NATURAL GAS AND KAOLIN
SORBENT AND ADDITIVES	100% $CaCO_3$	95% $CaCO_3$ 5% $NaHCO_3$	94% $CaCO_3$ 5% $NaHCO_3$ 1% Li_2CO_3	94% $CaCO_3$ 5% $NaHCO_3$ 1% Li_2CO_3	100% $CaCO_3$	95% $CaCO_3$ 5% $NaHCO_3$	94% $CaCO_3$ 5% $NaHCO_3$ 1% Li_2CO_3	94% $CaCO_3$ 5% $NaHCO_3$ 1% Li_2CO_3
Ca/S RATIO	1.7	1.7	1.7	1.7	2.2	1.6	1.7	1.7
BASELINE SO_2	2736	2641	2686	2667	2364	2706	2624	2665
REFERENCE	C751-73, -76	C751-82, -85, -124	C795-4, -6, -8	C795-15	C482-132, -133	C751-94, -95	C795-9, -10	C795-12

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Figure 23. Comparison of Vicron limestone with sodium bicarbonate promoters injected at the burner and at S-4.

Effect of Fly Ash Injection and Sodium Promotion on Sulfur Capture with Vicron Limestone in SO_2-Doped Natural Gas--

The objectives of this work were:

- To examine the effect of fly ash injection on the sulfur capture obtained with Vicron limestone in an SO_2-doped gas flame (i.e., to see if an ash-sorbent interaction was produced in the SRI combustor).
- To further examine the effectiveness of sodium bicarbonate as a promoter of sulfur capture.
- To determine the effect of fly ash on the effectiveness of the sodium bicarbonate promoter.
- To collect solids samples under the above conditions, and to examine the samples under the SEM to gain insight into the process mechanisms.

The sulfur capture tests were performed with the Vicron limestone injected through the core of the burner. The burner with mechanically adjustable swirl vanes was used for this work. A 30° swirl angle was used, with no staging. The combustor was fired at full load (1.06 GJ/hr or 1 x 10^6 Btu/hr) during all tests. Under these conditions, the maximum gas temperatures (determined using the HVT) at various furnace locations were as follows:

Location		S-1	S-2	S-3	S-4
Temperature,	°C	1550	1375	1250	1150
	°F	2820	2510	2280	2100

Effect of fly ash injection on sulfur capture--Figure 24 shows the effect of fly ash injection on the sulfur capture obtained with Vicron 45-3 limestone. The operating conditions for these tests were as described previously, except that fly ash was injected with the natural gas and primary air during some of the tests. The fly ash was obtained from the ESP hoppers at the Gaston Plant located in Wilsonville, Alabama. The fly ash was reportedly generated from a medium-sulfur, bituminous coal. An analysis of the fly ash performed at SRI yielded the chemical composition shown in Table 16.

As shown in Figure 24, injection of the fly ash had the effect of increasing sulfur capture under these conditions. This was contrary to expectations because all previous data from other investigators had shown a reduction in sulfur capture with fly ash addition. Perhaps there is something unique about the Gaston fly ash, but there does not appear to be anything highly unusual in the chemical analysis of the ash. In order to further investigate this result, solids samples were collected with the PQP probe at S-5. These solids samples (Vicron limestone alone and Vicron limestone + ash) were characterized in terms of their BET surface areas and their sulfate and calcium contents. The results are summarized in Table 17. These results show that the fly ash injection reduced the BET surface area of the sorbent while increasing sorbent

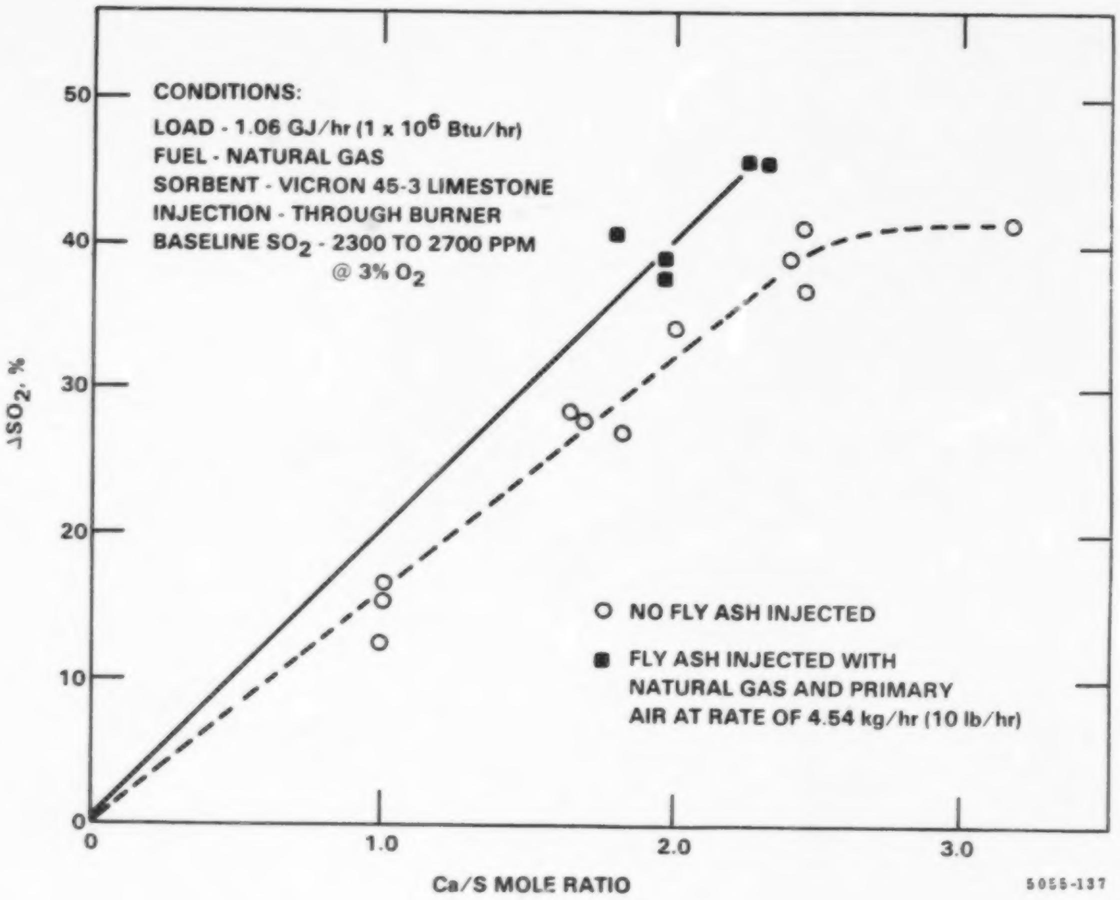


Figure 24. Effect of fly ash injection on the sulfur capture obtained with Vicron 45-3 limestone.

TABLE 16. CHEMICAL COMPOSITION OF GASTON FLY ASH USED IN FURNACE TESTS

Oxide	Weight %[a]
Li_2O	0.08
Na_2O	0.46
K_2O	2.5
MgO	1.2
CaO	2.8
Fe_2O_3	14.2
Al_2O_3	27.3
SiO_2	47.9
TiO_2	1.9
P_2O_5	0.83
SO_3	0.63
LOI	5.3

a. All analyses performed on ignited sample.

TABLE 17. BET SURFACE AREAS AND SULFATE AND CALCIUM CONTENTS OF SOLIDS SAMPLES EXTRACTED AT S-5 WITH PQP PROBE[a]

Sample No. (C795-)	Sample type[b]	BET area (m^2/g)	Weight % SO_4^{-2}	Weight % CaO	Utilization[c] (%)
45	V	6.8	12.7	71.1	10.4
48	V	6.8	12.1	71.1	9.9
51	V	7.3	11.5	71.1	9.4
68	V+A	2.0	15.1	41.1	21.4
71	V+A	1.9	16.4	41.1[d]	23.3

a. Weight percent SO_4^{-2} and CaO on as-received basis.

b. V = Vicron limestone alone; V+A = Vicron limestone + ash.

c. Reduction in gas-phase SO_2 at the system exit gave apparent utilizations for Vicron limestone and Vicron limestone + ash of 16 and 20%, respectively (at Ca/S = 2).

d. Assumed from analysis of preceding sample.

utilization. Note that the utilizations given in Table 17 are somewhat lower than those calculated from the gas phase ΔSO_2 because the reaction is not complete at S-5. Although S-5 samples show a factor of two increase in utilization with ash, gas-phase ΔSO_2 measurements show only about a 25% increase.

The results given in Table 17 suggest that the fly ash may be acting as a flux to promote product layer diffusion. Alternatively, the fly ash may be influencing ionic diffusion without fluxing the sorbent, as suggested by Borgwardt (11).

Effect of sodium bicarbonate on sulfur capture--These tests were conducted under the same conditions described above, except that sodium bicarbonate, $NaHCO_3$, was added to the Vicron limestone to form a mixture of 5 wt % $NaHCO_3$ and 95 wt % Vicron limestone. The $NaHCO_3$ and Vicron limestone were mixed by tumbling in a bucket, and the mixture was injected through the burner core in the same manner used with Vicron limestone alone.

The effect of $NaHCO_3$ on the sulfur capture is illustrated in Figure 25. The effect is obviously quite dramatic. For example, the sulfur capture obtained at a Ca/S mole ratio of 2 is almost double that obtained with Vicron limestone alone. Solids samples were again extracted to investigate the effect of $NaHCO_3$ on BET surface area and sorbent utilization. This time PQP samples were extracted at S-4, S-5, and SD-2. The surface areas and analyses for these samples are given in Table 18. The utilizations indicated for the SD-2 samples may be high due to a nonrepresentative amount of the sodium promoter in these samples, or due to in-probe reactions. These results suggest that the sorbent surface area is decreasing while the utilization is increasing as the sorbent passes through S-4 (ca. 2100°F) to SD-2 (ca. 1700°F). The solid utilization in the SD-2 sample is higher than expected based on the gas phase ΔSO_2 (about 47% versus about 30%). This may be due to additional pickup of SO_2 in the sampling probe.

The results given in Table 18 could be interpreted in terms of a fluxing mechanism in which diffusion is facilitated by creation of a molten product layer. SEM photomicrographs of $NaHCO_3$-promoted sorbent particles are shown in Figure 26. These samples were taken from S-5 using the PQP sampling probe. Samples collected with and without SO_2 in the system are shown for comparison. These photographs do not show any significant change in morphology with the SO_2 reaction. However, these are relatively low resolution photographs, and a relatively thick (~200 Å) gold coating was used. This could cause some of the surface features to be obscured. In any case, these photographs do not show the kind of fluxing or fusion that has been found in chromium-promoted sorbent samples (12).

Effect of fly ash and sodium bicarbonate combined--In this test both fly ash and $NaHCO_3$ were used simultaneously at the same levels given previously. This was done to determine if the presence of the fly ash would be deleterious to the activity of the $NaHCO_3$ promoter. As shown in Figure 27, the results suggest that the fly ash is deleterious to the $NaHCO_3$, even though the fly ash alone acts as a promoter. The sulfur captures obtained with fly ash and $NaHCO_3$

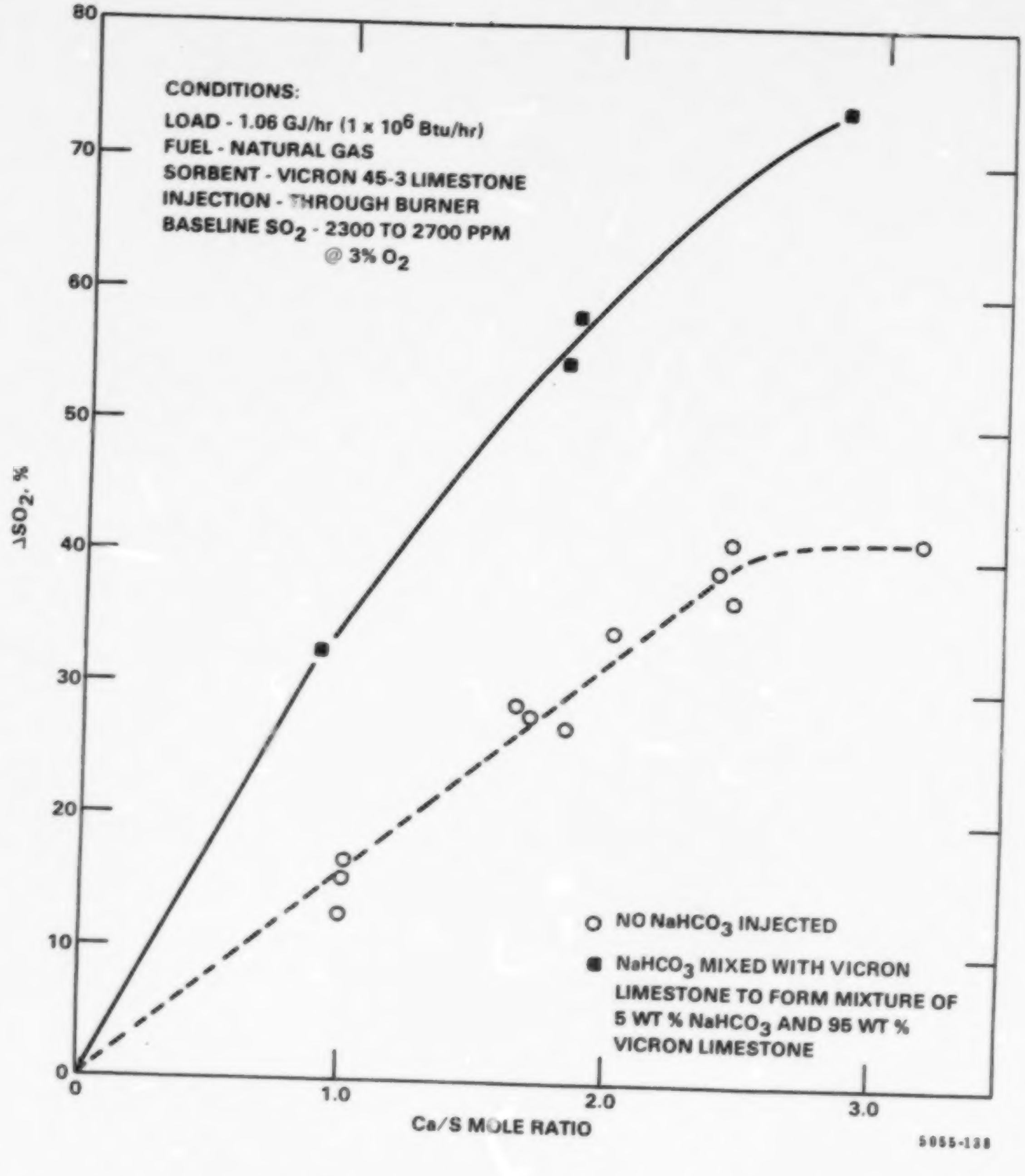


Figure 25. Effect of sodim bicarbonate on the sulfur capture obtained with Vicron 45-3 limestone.

TABLE 18. BET SURFACE AREAS AND SULFATE AND CALCIUM CONTENTS OF SOLIDS SAMPLES WITH $NaHCO_3$ ADDED TO VICRON LIMESTONE

Sample No. (C795-)	Sample location	BET area (m^2/g)	Weight % Na_2O^a	Weight % SO_4^{-2b}	Weight % CaO^b	Utilization^c (%)
104	S-4	4.9	2.1	20.4	65.3	18.2
106	S-4	5.4	2.1	21.3	65.3	19.0
92	S-5	3.9	1.7	29.8	62.9	27.1
97	S-5	4.1	1.7	29.2	62.9	27.1
100	SD-2	--[d]	3.8	43.4	52.5	48.2[e]
102	SD-2	--[d]	3.8	45.9	55.2	48.5[e]

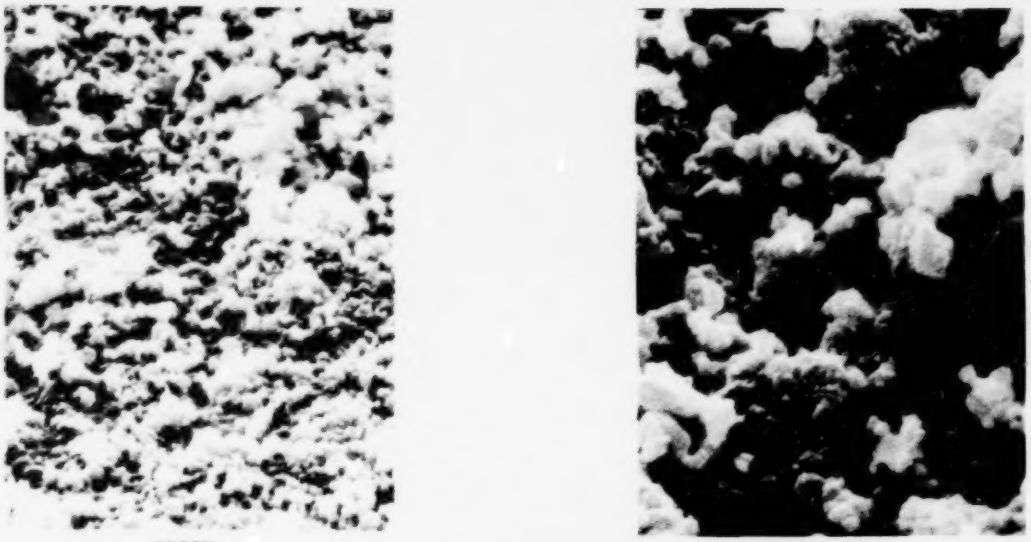
a. Ignited basis.

b. As-received basis.

c. Utilization = (wt % SO_4^{-2})(56)/(wt % CaO)(96)

d. Insufficient sample for BET analysis.

e. Utilization may be high due to nonrepresentative amount of sodium in sample or due to in-probe reaction.



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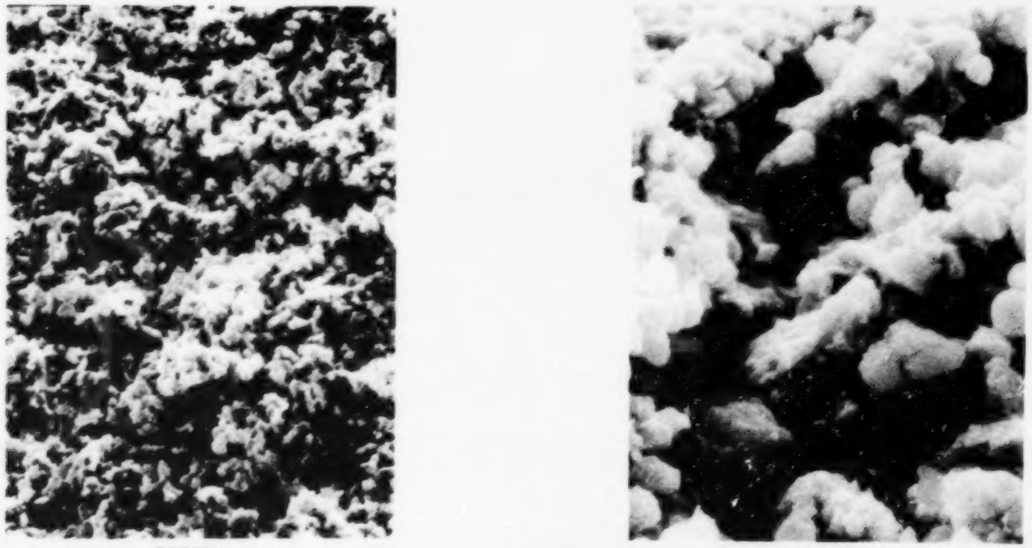
WITHOUT SO_2 IN SYSTEM



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WITH SO_2 IN SYSTEM

Figure 26. SEM photomicrographs of $NaHCO_3$-promoted sorbent particles extracted at S-5.

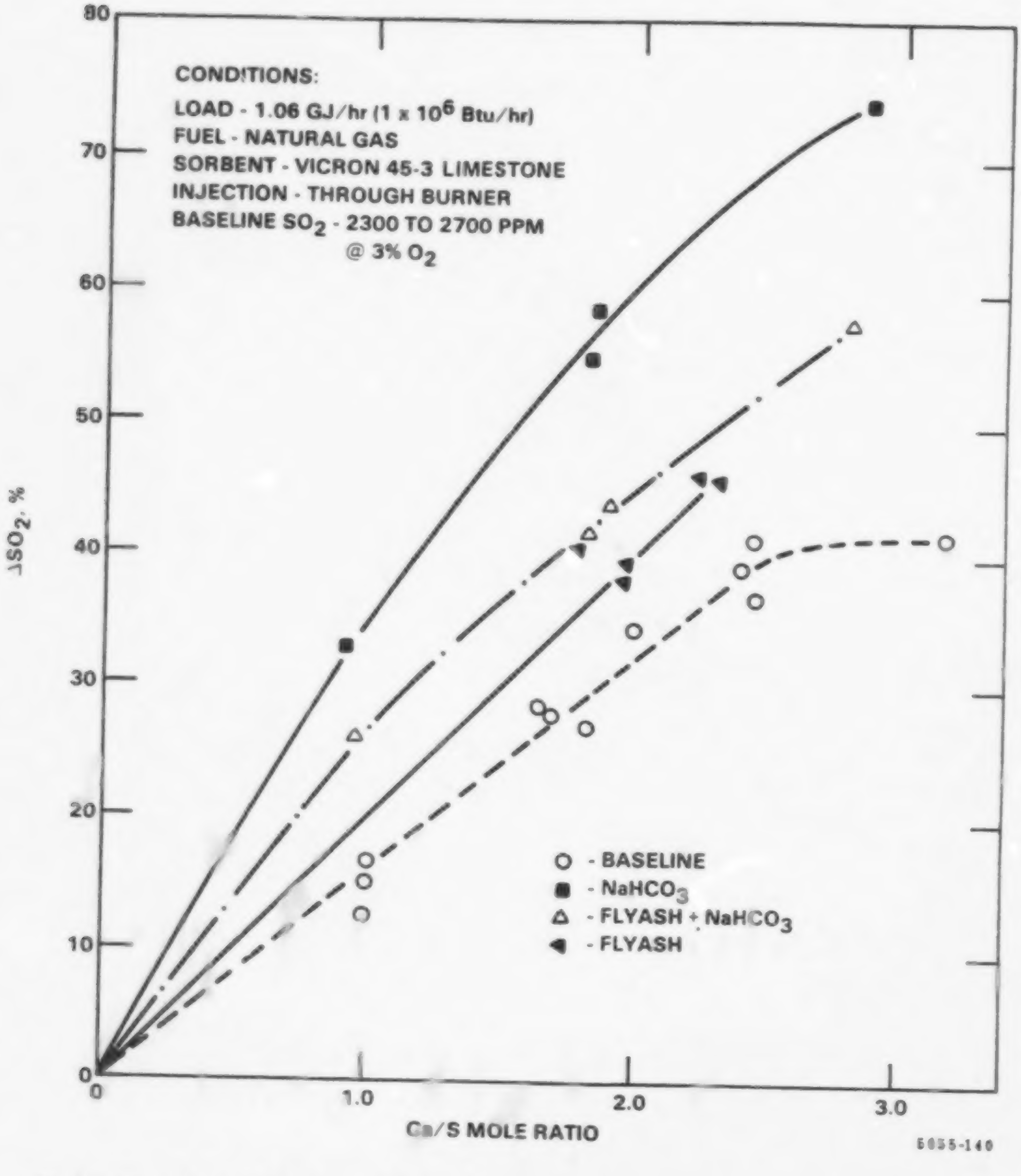


Figure 27. Effect of fly ash and $NaHCO_3$ combined on the sulfur capture obtained with Vicron 45-3 limestone.

combined lie between the captures obtained with $NaHCO_3$ alone and with fly ash alone. The BET surface areas of two samples extracted at S-5 were the same as those extracted from the same location with fly ash alone, but only half of the values obtained with $NaHCO_3$. The utilizations (based on solids analyses) were slightly higher than with fly ash alone, but slightly lower than with $NaHCO_3$ alone. A comparison of the various solids analyses is given in Table 19.

An SEM photograph and energy dispersive X-ray (EDX) scans of a Vicron limestone-fly ash-$NaHCO_3$ mixture collected in the resistivity probe cavity at about 149°C (300°F) are shown in Figure 28. A number of spherical (presumably) fly ash particles are shown, some of which are shown to be fly ash by the EDX scan for silicon. Numerous small fragments near the center of the photograph appear to be sorbent fragments based on the calcium scan. The large clump on the right side appears to be mainly composed of fly ash.

There are a number of remaining unanswered questions concerning the effects of fly ash and promoter including:

- Are wall effects a factor?
- Why does the degree of agreement between gas phase ΔSO_2 measurements and solids analysis vary?
- Which measurement (gas-phase or solids) is correct?

Evaluation of sodium promotion with deep-cleaned versus raw coal--These tests were conducted in order to determine whether the effectiveness of the sodium promoter could be improved by removing some of the coal ash prior to combustion. This concept was based on the belief that the lack of success with sodium promotion when coal was fired was due to the condensation of the volatilized sodium on ultrafine ash particles. These particles could account for a relatively large portion of the total surface area available for condensation.

This hypothesis was tested by conducting standard ΔSO_2 tests with sodium-promoted Vicron limestone injected at the burner while firing Homer City raw and deep-cleaned coals. The raw coal contained 17 to 21% ash and 1.6 to 2.3% sulfur compared to 7 to 8% ash and 1.2 to 1.3% sulfur in the deep-cleaned coal. The raw coal and deep-cleaned coal were fired at rates of 36.3 and 31.8 kg/hr (80 and 70 lb/hr), respectively, in order to yield equivalent nominal heat release rates of 1.06 GJ/hr (1×10^6 Btu/hr). The sodium-promoted Vicron was prepared by mixing 95% by weight Vicron and 5% by weight sodium bicarbonate.

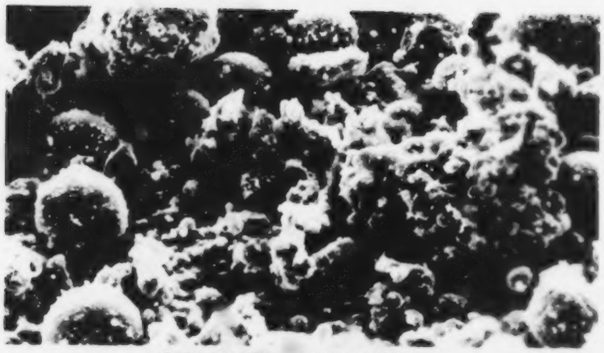
The results of these tests are summarized in Figure 29. All of these data were obtained with the Vicron limestone (or Vicron limestone + sodium mix) injected through the burner. The promoter appeared to be slightly effective with the raw coal, but ineffective with the deep-cleaned coal. In fact, the promoter actually appeared to have a negative impact on the sulfur captures obtained with the deep-cleaned coal at Ca/S ratios beyond 3. This could be partially due to uncertainties in the experimental data. The difference in SO_2 captures between the raw versus deep-cleaned coal can be attributed in part to

TABLE 19. COMPARISON OF SOLIDS EXTRACTED AT S-5

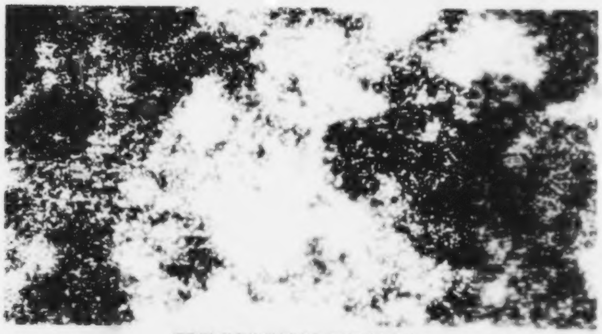
	BET area (m^2/g)	Utilization based on solids analysis[a] (%)	Utilization based on gas-phase ΔSO_2[b] (%)
Vicron	7.0 (± 0.3)	9.9 (± 0.5)	15-17
Vicron + ash	1.95 (± 0.05)	21.4 (± 1.0)	20
Vicron + $NaHCO_3$	4.0 (± 0.1)	24.2 (± 0.2)	31
Vicron + both	2.1 (± 0.1)	22.7 (± 1.5)	22.5

a. Solids extracted using PQP at S-5.

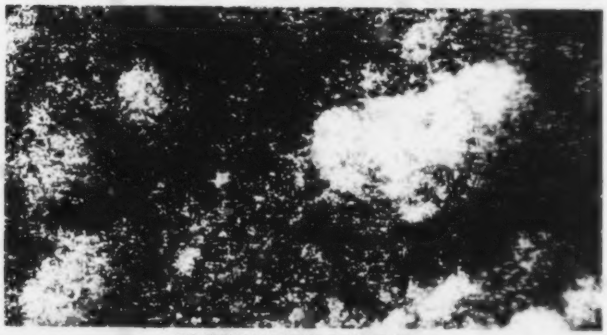
b. Based on reduction of gas-phase SO_2 at system exit (~260°C or 500°F) at Ca/S = 2.



SEM PHOTOGRAPH-2000X



EDX SCAN FOR CALCIUM



EDX SCAN FOR SILICON

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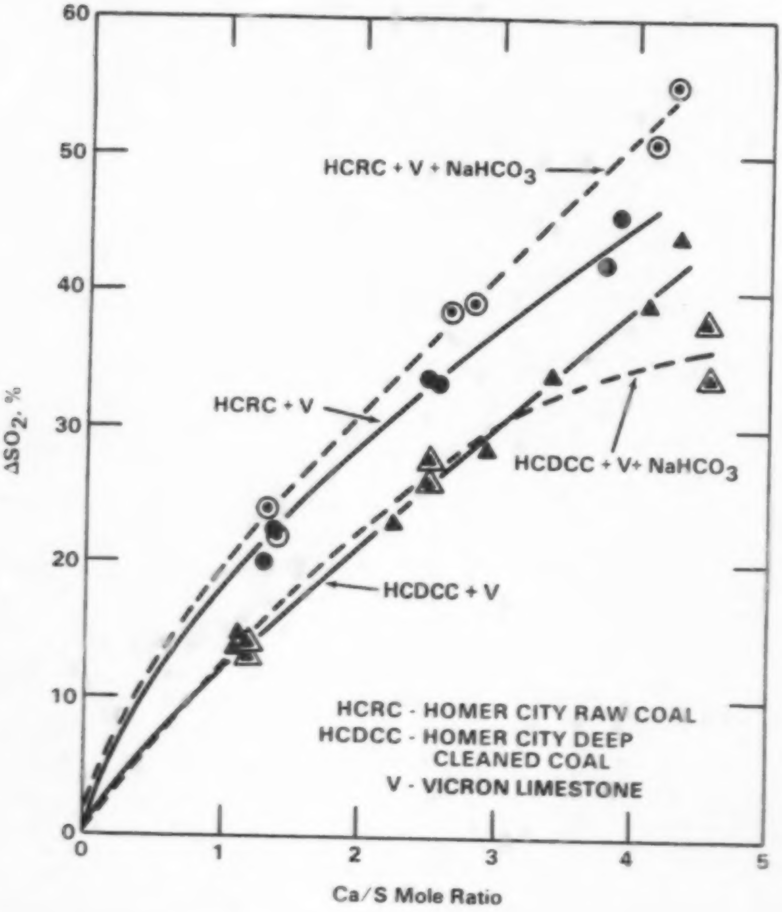
Figure 28. SEM photograph and EDX scans of sorbent-fly ash-$NaHCO_3$ mixture.



a. NOTE: PROMOTED AND NON-PROMOTED SORBENT INJECTED THROUGH BURNER. PROMOTER ADDED TO FORM MIXTURE OF 5 WT % $NaHCO_3$/95% VICRON LIMESTONE.

621-439

Figure 29. Effect of the raw coal versus deep-cleaned coal on the effectiveness of sodium promoter.

the difference in baseline SO_2 levels. The baseline SO_2 levels are given below:

Homer City raw coal + Vicron limestone	1930 ± 46 ppm
Homer City raw coal + Vicron limestone + $NaHCO_3$	1775 ± 54 ppm
Homer City deep-cleaned coal + Vicron limestone	847 ± 8 ppm
Homer City deep cleaned coal + Vicron limestone + $NaHCO_3$	718 ± 79 ppm

SECTION 3

STUDIES OF PARTICULATE PROPERTIES AND ELECTROSTATIC PRECIPITATOR (ESP) PERFORMANCE

EQUIPMENT AND PROCEDURES

In Situ Resistivity Probe

A modified version of the SRI point-plane resistivity probe was used to obtain in situ resistivity data. The in situ resistivity test methods have been described by Nichols and Banks (13). The resistivity was calculated from the voltage drop across the precipitated dust layer and the electrical current density through the layer immediately prior to electrical breakdown.

Laboratory Resistivity Cell

Samples of fly ash alone and mixtures of fly ash in combination with reacted sorbent were taken from the cavity of the in situ resistivity probe for laboratory analysis. The samples were placed in ASME PTC-28 test cells and heated to 450°C (842°F) in air containing 8% by volume water vapor. The oven was then turned off and the resistivity was determined as a function of descending temperature over the range of 450 to 85°C (842 to 185°F). These measurements were made in accordance with IEEE Standard 548-1981.

For measurements made with SO_3 in the environment, the samples were placed in a radial resistivity test cell designed by Bickelhaupt (14). The cell was placed in an oven and maintained at a constant temperature near 150°C (302°F). Air containing 8% moisture and a known level of SO_3 was passed over the test cell, and the resistivity was monitored until an equilibrium condition was attained. The result obtained by this method represents the minimum resistivity value that can be attained in flue gas containing the prescribed level of SO_3. The in situ resistivity will be higher than the laboratory value if the dynamic interaction of the particulate and SO_3 in the flue gas does not approach the equilibrium situation.

Particle Size Distribution Measurements

Particle size distribution measurements were made using a combination of modified Brink Model BMS-11 Cascade Impactors, a Thermo-Systems Model 3030 Electrical Aerosol Size Analyzer, and a Climet Model C1-208C Optical Particle Counter. The general procedure for the use of cascade impactors has been described by Harris (15). The Brink impactors used in this study were equipped with a precutter cyclone, six impactor stages, and a backup filter. Light-weight glass fiber substrates were used on the impaction stages. The impactor was inserted into the flue gas stream and allowed to reach gas temperature before beginning the impactor sampling. The sampling rate was adjusted to sample isokinetically with the centerline velocity at the resistivity port. Each set of impactor measurements (with and without sorbent) consisted of 12 impactor runs, 2 of which were blank runs. The blank runs were performed with a filter ahead of the impactor, so that any substrate weight changes caused by flue gas-substrate interaction could be quantified and taken into account. The blank corrections were generally quite small compared to the particulate mass collected on the impaction stages. The raw impactor data were reduced using the Cascade Impactor Data Reduction System (CIDRS) developed by Johnson et al. (16,17). This yields size distribution data for particles in the range of 0.5 to 10 μm.

For finer particles in the range of 0.01 to 0.5 μm, it was necessary to use an electrical aerosol size analyzer (EASA) in combination with an optical particle counter (OPC). The operating principles of these instruments have been reviewed by Liu and Pui (18) and Liu et al. (19). These instruments are designed to handle relatively low particulate concentrations at room temperature. Therefore, the sample to be analyzed must be extracted from the flue gas, cooled, and diluted prior to examination in the EASA or OPC. The sample extraction and dilution system that was used in this study has been described by Felix et al. (20). Extensive testing has been done to verify that secondary aerosols are not produced in the sample extraction and dilution system. The EASA and OPC data were obtained concurrently with the impactor data. All three data sets were combined to form a complete size distribution over the range of 0.01 to 10 μm, with and without sorbent injection.

SO_3 Sampling Apparatus

Measurements of the gas-phase SO_3 concentrations were made by the modified controlled-condensation technique described by Cheney and Homolya (21). A quartz wool plug was used to remove particulate ahead of the SO_3 condenser. The quartz wool plug was maintained at 274°C (525°F) to prevent uptake of SO_3 on the particulate collected on the plug. This has been found to be satisfactory in sampling ash-laden flue gas from coal-fired boilers (21). However, the loss of SO_3 to the particulate may be a problem in the presence of reactive sorbent. Therefore, the SO_3 data reported here must be regarded as lower limits on the levels actually present in the flue gas.

SO_3 Conditioning System

An SO_3 conditioning system was fabricated and installed in the SRI coal combustion facility. The system is basically a miniature Wahlco converter in which SO_3 is produced by the catalytic oxidation of SO_2. The SO_2 is allowed to flow out of a pressurized cylinder of the pure gas through a regulator and a rotameter before being blended with a metered amount of air just ahead of the converter. The converter itself consists of a 0.457-m (1.5-ft) length of 2.54-cm (1-in.) schedule 40 stainless steel pipe packed with about 200 cm^3 of V_2O_5 catalyst, which was supplied by Wahlco, Inc. The pipe is wrapped with electrical resistance heaters and insulation so that the temperature inside the converter can be maintained within the range of about 371 to 482°C (700 to 900°F). Under these conditions, conversion efficiencies of 98 to 99% have been confirmed by SO_3/SO_2 measurements at the inlet and outlet of the converter. Over the range of conditions studied, the conversion was essentially complete regardless of flow rate.

The SO_3 is injected into the flue gas through a right-angle nozzle inserted through the duct wall. The injection line is well insulated to prevent condensation of the SO_3. The converter is typically operated with a nominal air flow rate of 6 L/min (0.21 ft^3/min), and the SO_2 flow is adjusted to achieve the desired injection rate. Even with the highest SO_2 flow, this flow rate of air was sufficient to provide 3 times the stoichiometric oxygen requirement for the conversion reaction. Thus, the conversion was always essentially complete. The difference between the metered SO_2 in the feed and the measured SO_3 in the converter discharge was never greater than 16%.

VALIDATION OF FLY ASH SIMULATION CAPABILITIES

For the first experiments, a low-sulfur, low-sodium coal, for which an extensive data base was available, was chosen for the fuel. This coal source (South African) was used during an evaluation performed by SRI of sodium conditioning for a hot-side ESP (22). Figure 30 compares laboratory resistivity measurements for the ash obtained from the combustor baghouse with those obtained from the full-scale plant burning coal from the same source. Also shown is a predicted curve based on the ash composition from the combustor sample. The ash composition obtained from the coal ash, from the combustor fly ash, and from the full-scale plant (Plant Lansing Smith of Gulf Power Company) are given in Table 20. These comparisons show good agreement between resistivity values obtained on ash samples from the pilot plant and the full-scale plant. The pilot plant fly ash exhibits a resistivity-temperature relationship which agrees with Bickelhaupt's (23) predictor. It should be noted that sulfur trioxide was not a factor in these measurements. Gas analyses on flue gas produced by the combustor indicated less than 0.5 ppm SO_3 at 149°C (~300°F) in the presence of ~400 ppm SO_2. No SO_3 was used in the laboratory environment.

Table 20 indicates that the combustor fly ash is similar in composition to that obtained during the full-scale field test. A comparison of the coal ash and fly ash chemical composition from the combustor trials indicates that the fly ash is almost identical in composition to the coal ash. This shows that composition-dependent wall losses in the combustor are not a problem for this coal source.

A large amount of experimental work has been conducted on the LIMB program using a high-sulfur Indiana coal, and therefore a supply of this fuel was obtained for experimental work at SRI. Proximate and ultimate analyses of this coal are given in Table 21. Figure 31 shows a comparison between laboratory-measured and predicted resistivity for the Indiana Lot No. 2 fly ash, with 8.1% water in air as the environment. Fly ash samples were obtained from the pilot-plant resistivity probe. All laboratory resistivity determinations were

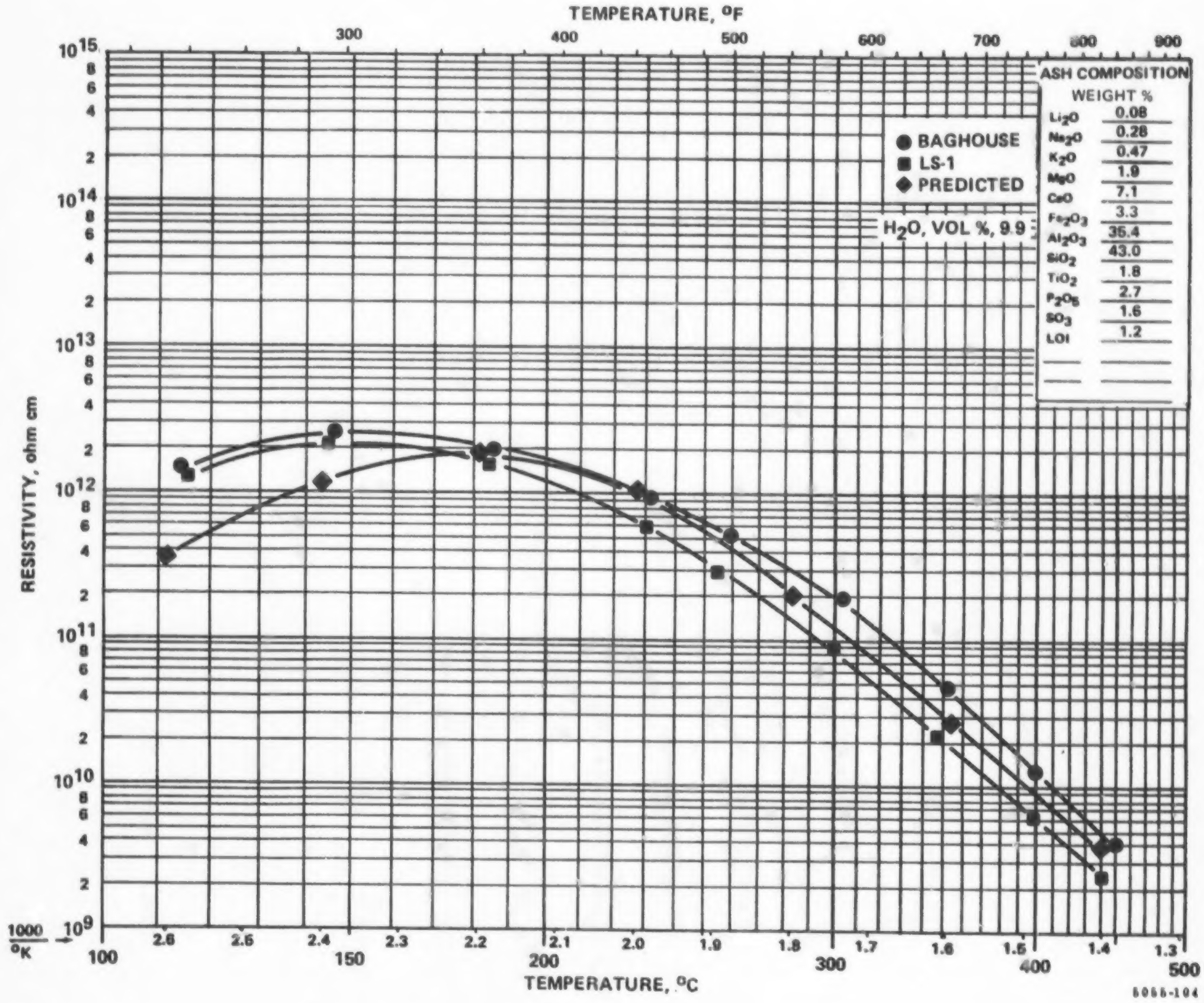


Figure 30. Fly ash resistivity comparison with South African coal.

TABLE 20. FLY ASH COMPOSITION COMPARISON

	Combustor trials		Full-scale plant sample
	Coal ash[a]	Fly ash av	
% Li_2O	0.07	0.08	0.08
% Na_2O	0.27	0.28	0.32
% K_2O	0.47	0.47	0.44
% MgO	1.9	1.9	2.3
% CaO	7.3	7.1	8.8
% Fe_2O_3	3.6	3.3	5.6
% Al_2O_3	36.3	35.4	34.8
% SiO_2	43.8	43.0	39.4
% TiO_2	1.7	1.8	1.7
% P_2O_5	2.8	2.7	2.9
% SO_3	0.3	1.6	0.9
% LOI	6.1	1.2	12.4

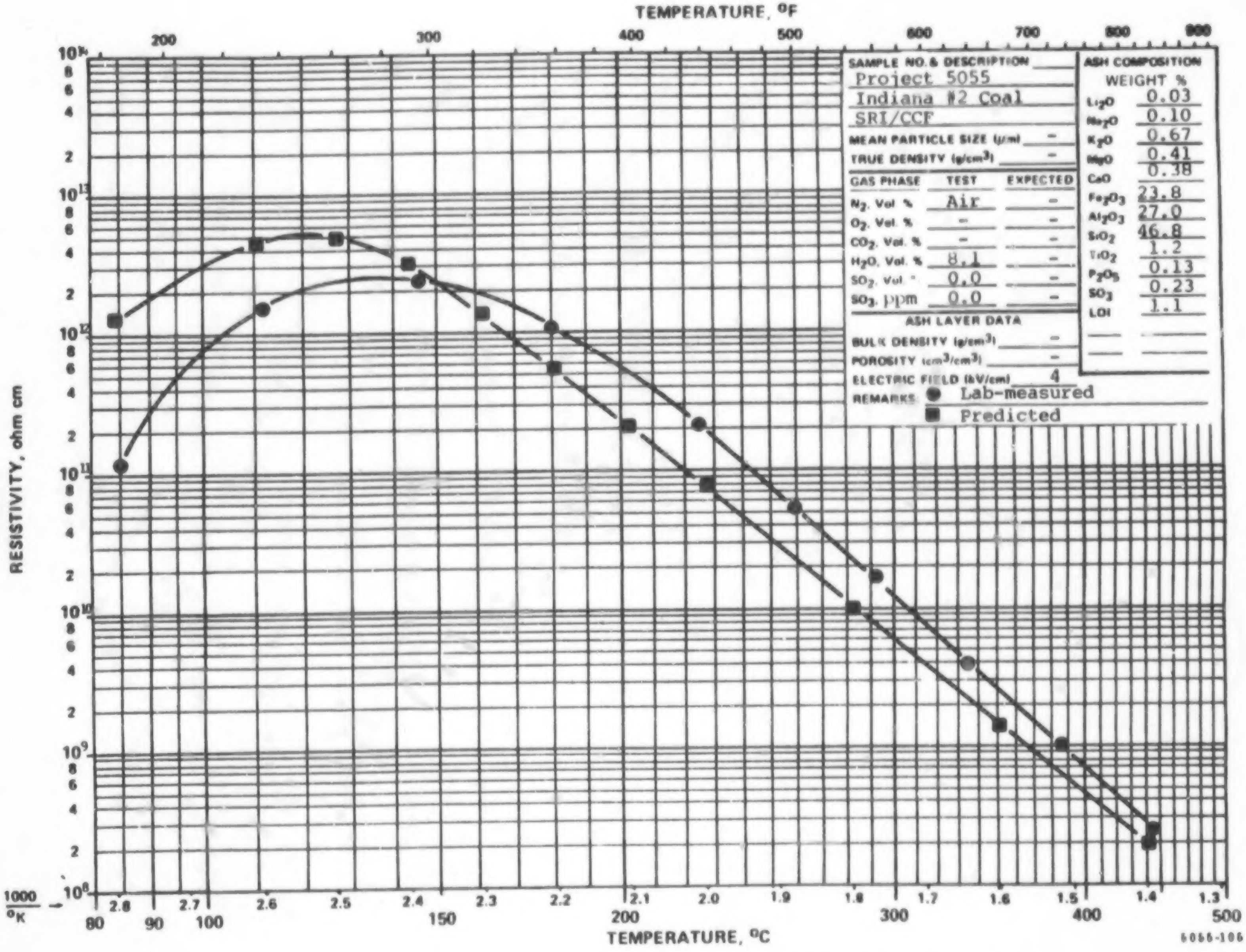
a. Ignited at 1100°C (2012°F).

b. Analyses performed on ignited samples.

TABLE 21. PROXIMATE AND ULTIMATE ANALYSES OF INDIANA LOT NO. 2 COAL

	Weight %
Proximate	
Moisture	8.92
Ash	7.56
Volatile matter	34.23
Fixed carbon	49.29
Btu/lb	12,146
Sulfur	2.29
Ultimate	
Moisture	8.92
Carbon	68.02
Hydrogen	0.97
Chlorine	0.43
Sulfur	2.29
Ash	7.56
Oxygen[a]	7.39

a. Oxygen determined by difference.



SAMPLE NO. & DESCRIPTION
Project 5055
Indiana #2 Coal
SRI/CCF
MEAN PARTICLE SIZE (μm) -
TRUE DENSITY (g/cm³) -

GAS PHASE	TEST	EXPECTED
N_2, Vol. %	Air	-
O_2, Vol. %	-	-
CO_2, Vol. %	-	-
H_2O, Vol. %	8.1	-
SO_2, Vol. %	0.0	-
SO_3, ppm	0.0	-

ASH LAYER DATA
BULK DENSITY (g/cm³) -
POROSITY (cm³/cm³) -
ELECTRIC FIELD (kV/cm) 4
REMARKS ● Lab-measured
■ Predicted

ASH COMPOSITION	WEIGHT %
Li_2O	0.03
Na_2O	0.10
K_2O	0.67
MgO	0.41
CaO	0.38
Fe_2O_3	23.8
Al_2O_3	27.0
SiO_2	46.8
TiO_2	1.2
P_2O_5	0.13
SO_3	0.23
LOI	1.1

Figure 31. Comparison of predicted and measured resistivity with Indiana Lot No. 2 coal.

performed in accordance with IEEE Standard 548-1981, using the decending temperature technique. While the comparison of predicted with measured resistivity does reveal differences, the two values never differ by more than a factor of two within the range of temperatures associated with cold-side and hot-side ESP's. It should be noted that the coal ash composition is unusual, with both the sodium and potassium concentrations only 25 to 30% of the values usually observed for fly ashes from Eastern bituminous coals.

Figure 32 shows a family of curves generated with Bickelhaupt's (23) revised model using Indiana No. 2 ash samples, and laboratory data for an air environment containing 21 ppm of SO_3 and 8.1% by volume water vapor. Good agreement is obtained between measured and predicted results. Similar agreement was obtained between predicted and measured results with an air environment containing 7 ppm SO_3 and 8.1% water vapor. In situ data obtained with the Indiana ash gave resistivity values of about 1×10^{10} ohm cm at 300°F in the presence of 25 to 30 ppm SO_3, whereas the equilibrium laboratory values were more than an order of magnitude lower in the presence of 21 ppm of SO_3. These results indicate that equilibrium conditions were not being approached in the combustion system resistivity probe under the conditions of these experiments. Equilibrium values have been more closely approached in the combustor when water-cooled heat exchangers were employed to reduce the gas temperature at the resistivity port, or when an isothermal residence chamber was installed prior to the resistivity probe. The laboratory results, however, strongly suggest that the combustor produces fly ash with resistivity characteristics consistent with those predicted from a correlation developed from a relatively large data base of ash samples obtained from full-scale plants.

The size distribution simulation capability of the pilot plant was evaluated by comparing the results from impactor measurements performed on the combustor with results from field measurements using identical instruments (Brink impactors). Figure 33 compares cumulative mass loadings obtained from the Lansing Smith plant and from the combustor using two different grinds of coal from the same source. This comparison indicates very good agreement between the pilot-plant and full-scale data sets with a "coarse" coal grind (50 to 60% through 200 mesh), and fair agreement with a "fine" coal grind (85 to 90% through 200 mesh) used as a fuel source. Figure 34 shows SEM photomicrographs of fly ash collected on Stage 3 of the Brink impactor used for sampling at both locations. The photomicrograph shows that the combustor was producing spherical ash particles typical of those produced by full-scale pulverized coal boilers. It should be noted that impactor sampling was performed at ~316°C (~600°F) since a hot-side ESP is installed at the Lansing Smith plant.

Size distribution measurements were also performed with the Indiana Lot No. 2 coal. Although total fly ash concentration measurements indicated that only about 37% of the coal ash was sampled by the impactors, the upstream losses primarily consist of large particles (>10 μm diameter), which would not significantly affect the cumulative mass loadings resolved by impactors. This conclusion is supported by Figure 35, which compares the results from combustor sampling with Indiana coal with results from four power plants burning similar coals. This comparison suggests that the combustor is producing somewhat

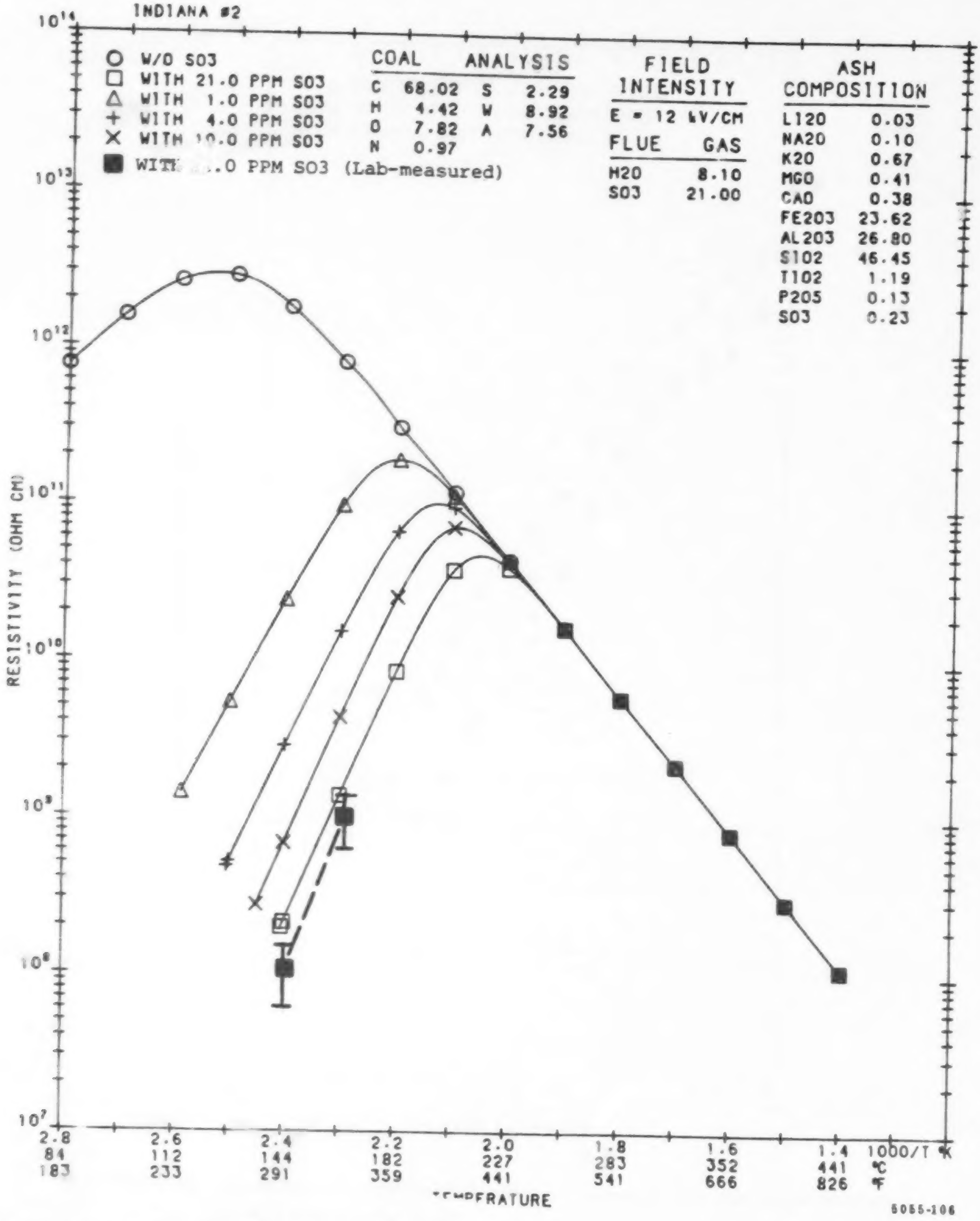


Figure 32. Comparison of predicted and measured laboratory resistivity with Indiana Lot No. 2 Coal.

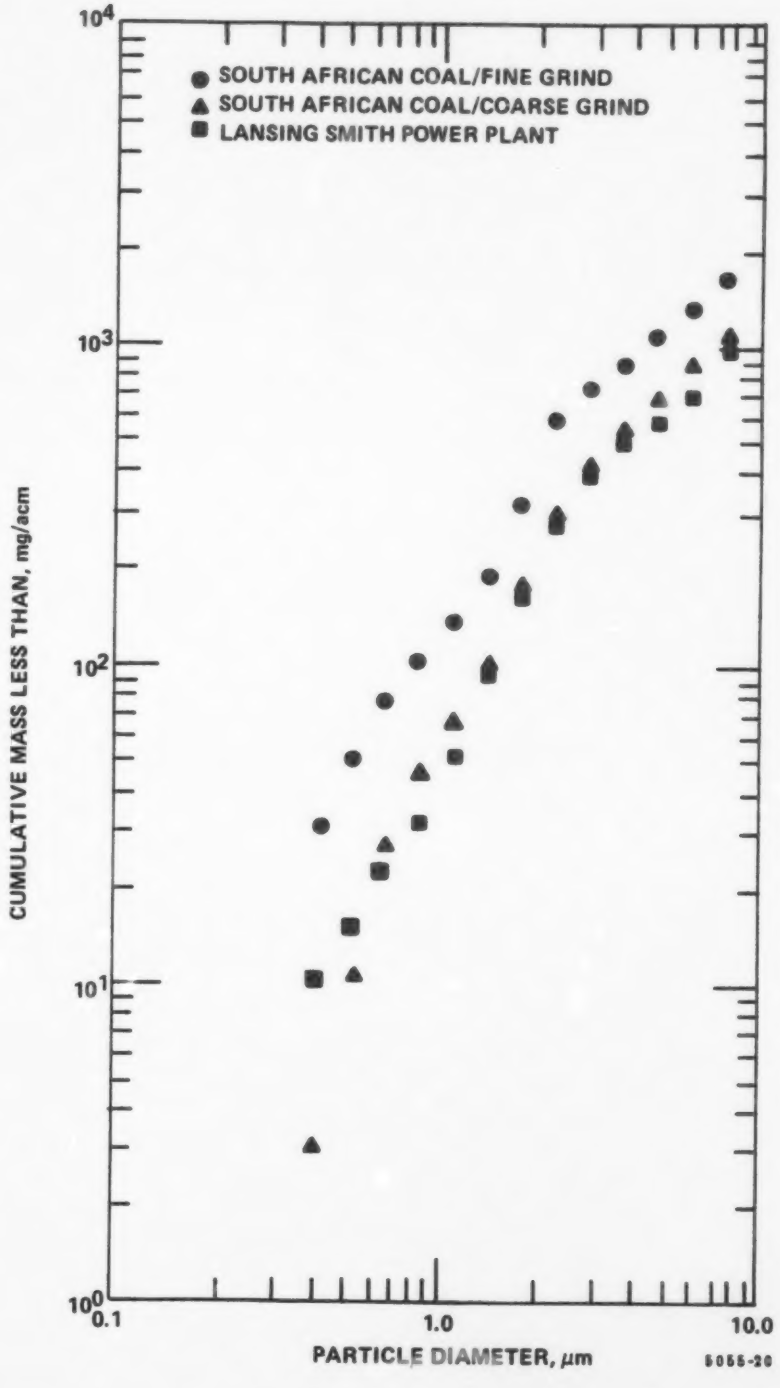


Figure 33. Comparison of size distributions from combustor with that obtained at the Lansing Smith power plant.

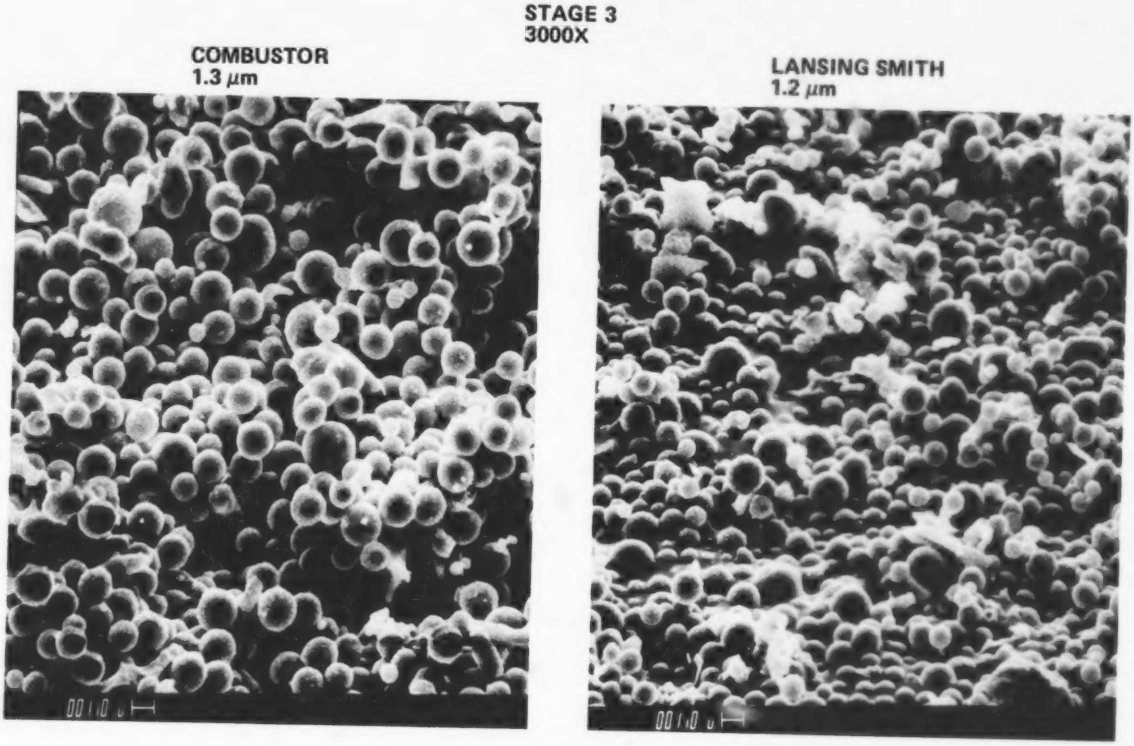


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Figure 34. SEM photomicrographs of fly ash collected on Stage 3 at SRI combustor and at the Lansing Smith power plant.

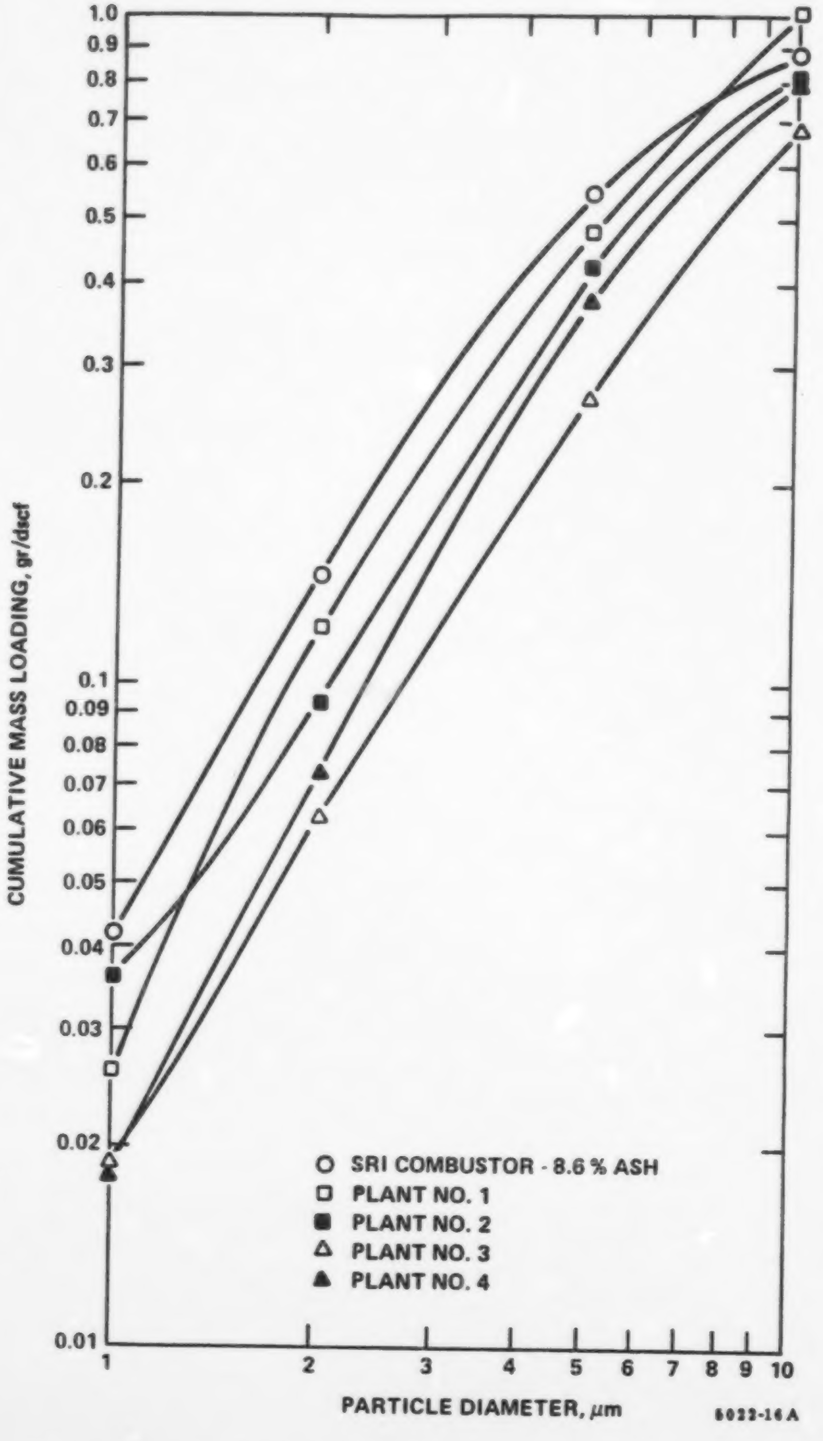

Figure 35. Size distributions from SRI combustor and various field tests.

higher concentrations of particles smaller than 10 μm, on an absolute concentration basis, than the full-scale plants.

If the cumulative mass loadings are converted to a cumulative percentage basis, it is necessary to adjust the cumulative percent from the combustor sampling to account for the dropout which occurs prior to the sampling point. This was accomplished by multiplying the cumulative percentages by the ratio of the predicted total mass loading to the measured value. The predicted total mass loading was obtained for the Indiana coal by using a least-squares fit of field test data developed by Dahlin and Altman (24). The results of this comparison are displayed in Figure 36, which shows that the combustor generated data, when adjusted for dropout, fall at the upper edge of the data sets for the four plants burning similar coals.

EFFECT OF SORBENT INJECTION ON ASH CHARACTERISTICS

Effect of Sorbent Injection on In Situ Resistivity

Since any furnace injection process will produce mixtures of fly ash and partially sulfated calcine, results obtained with Vicron limestone are expected to be at least qualitatively indicative of the effects of LIMB on ash collectability. Therefore, laboratory and in situ resistivity measurements were made to determine the effects of Vicron limestone injection on resistivity and to evaluate the response of the ash sorbent mixtures to SO_3 conditioning and moisture conditioning.

Figure 37 summarizes the in situ resistivity data obtained with the 2.3% sulfur Indiana bituminous coal with and without burner injection of Vicron limestone at a nominal calcium-to-sulfur ratio of 2:1. Table 22 gives the chemical compositions of the fly ash and the ash/sorbent mixture produced with the Indiana coal with and without Vicron limestone injection. No SO_3 was added to the flue gas. The SO_3 concentration variations shown without Vicron limestone addition were obtained by varying the flue gas cooling regime using the water-cooled heat exchangers ahead of the resistivity probe. The lowest level of SO_3 corresponded to the greatest amount of water cooling. For the measurements made with Vicron limestone addition, the SO_3 level was adjusted by varying the amount of excess air used in the furnace. An SO_3 level of <0.2 ppm corresponded to 2.2% O_2 in the flue gas, and an SO_3 level of 7.9 ppm corresponded to 6.5% O_2 in the flue gas.

Several observations can be made from an examination of Figure 37:

- The in situ data at the lower flue gas temperature without Vicron limestone approach the equilibrium resistivity values predicted by Bickelhaupt (23).
- If no residual SO_3 is present, ash/sorbent mixtures exhibit in situ resistivities of ~10^{12} ohm cm.

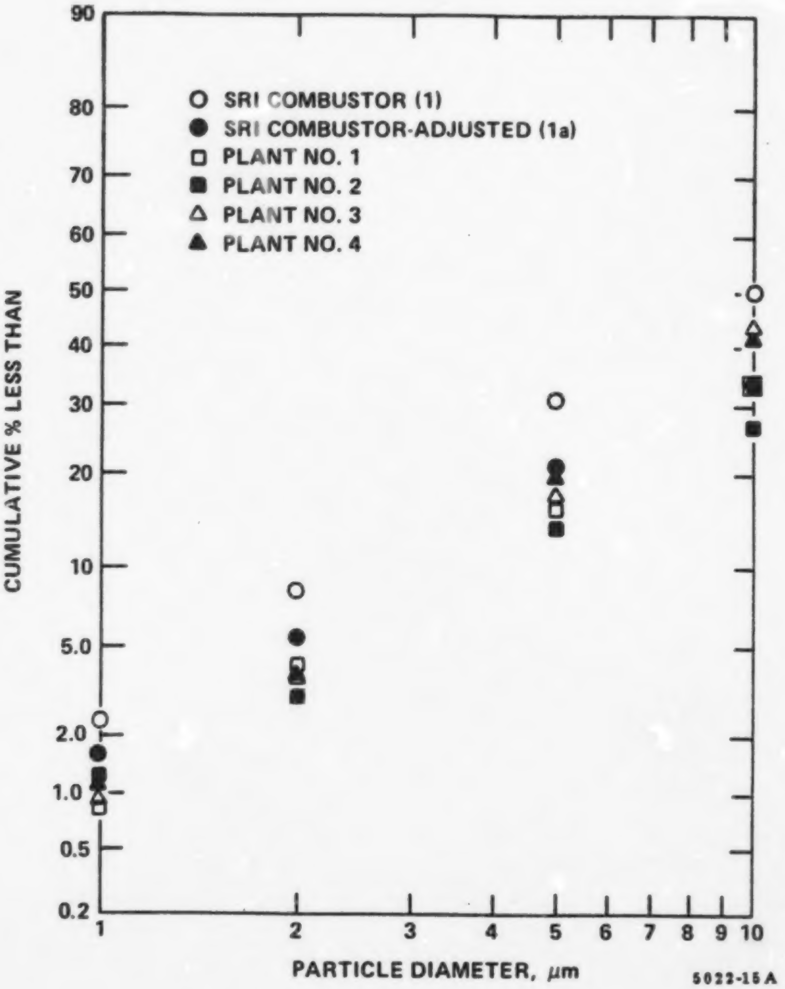

Figure 36. Size distributions from SRI combustor and various field tests.

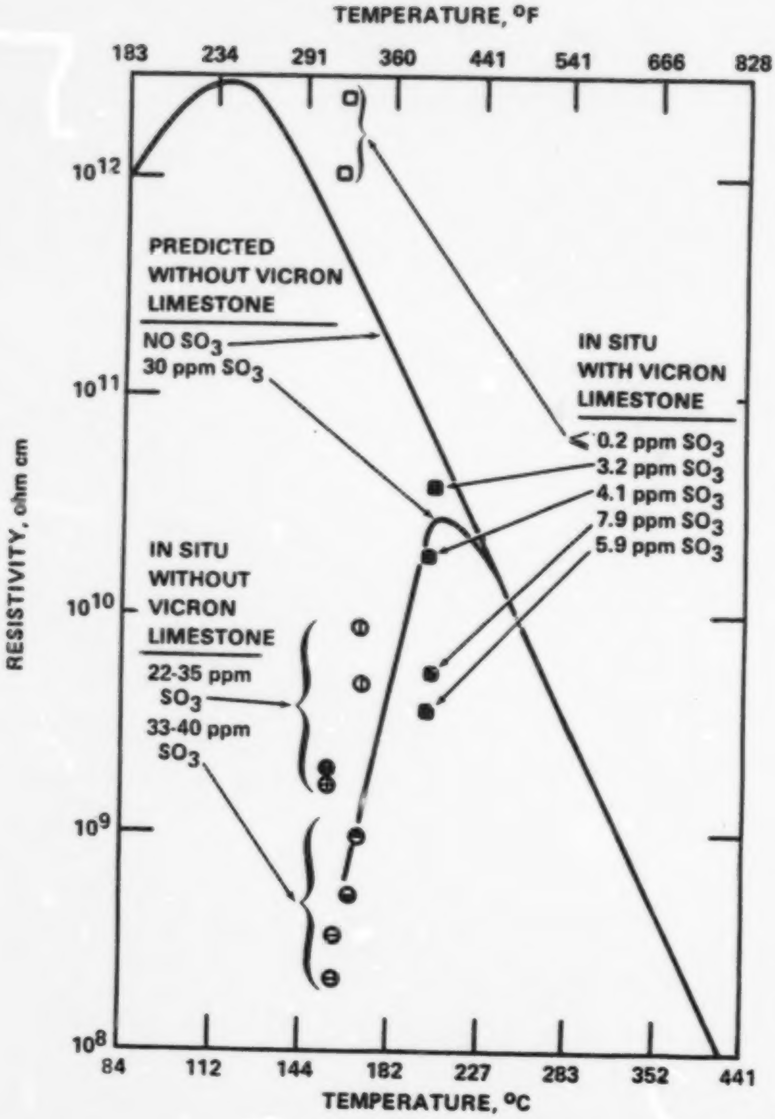

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Figure 37. Effect of burner injection of Vicron limestone on the in situ resistivity obtained with 2.3% sulfur Indiana bituminous coal.

TABLE 22. CHEMICAL ANALYSES OF FLY ASH AND FLY ASH/SORBENT MIXTURE PRODUCED FROM INDIANA COAL AND VICRON LIMESTONE

	Without Vicron limestone (Wt %)	With Vicron limestone (Wt %)
Li_2O	0.03	0.02
Na_2O	0.08	0.07
K_2O	0.59	0.35
MgO	0.19	0.44
CaO	0.28	39.4
Fe_2O_3	25.3	12.7
Al_2O_3	26.1	13.8
SiO_2	44.5	25.1
TiO_2	0.91	0.46
P_2O_5	0.07	0.03
SO_3	0.54	7.7

- Small residual SO_3 concentrations have a dramatic effect on the resistivity of ash/sorbent mixtures. The presence of the sorbent appears to increase the response of the fly ash to a given SO_3 concentration at relatively high flue gas temperatures (~199°C/390°F).

- Resistivity values in the range for good precipitator operation can be achieved for Vicron limestone/ash mixtures in the presence of relatively low residual SO_3 concentrations, when the source of SO_3 is oxidation of naturally occurring SO_2.

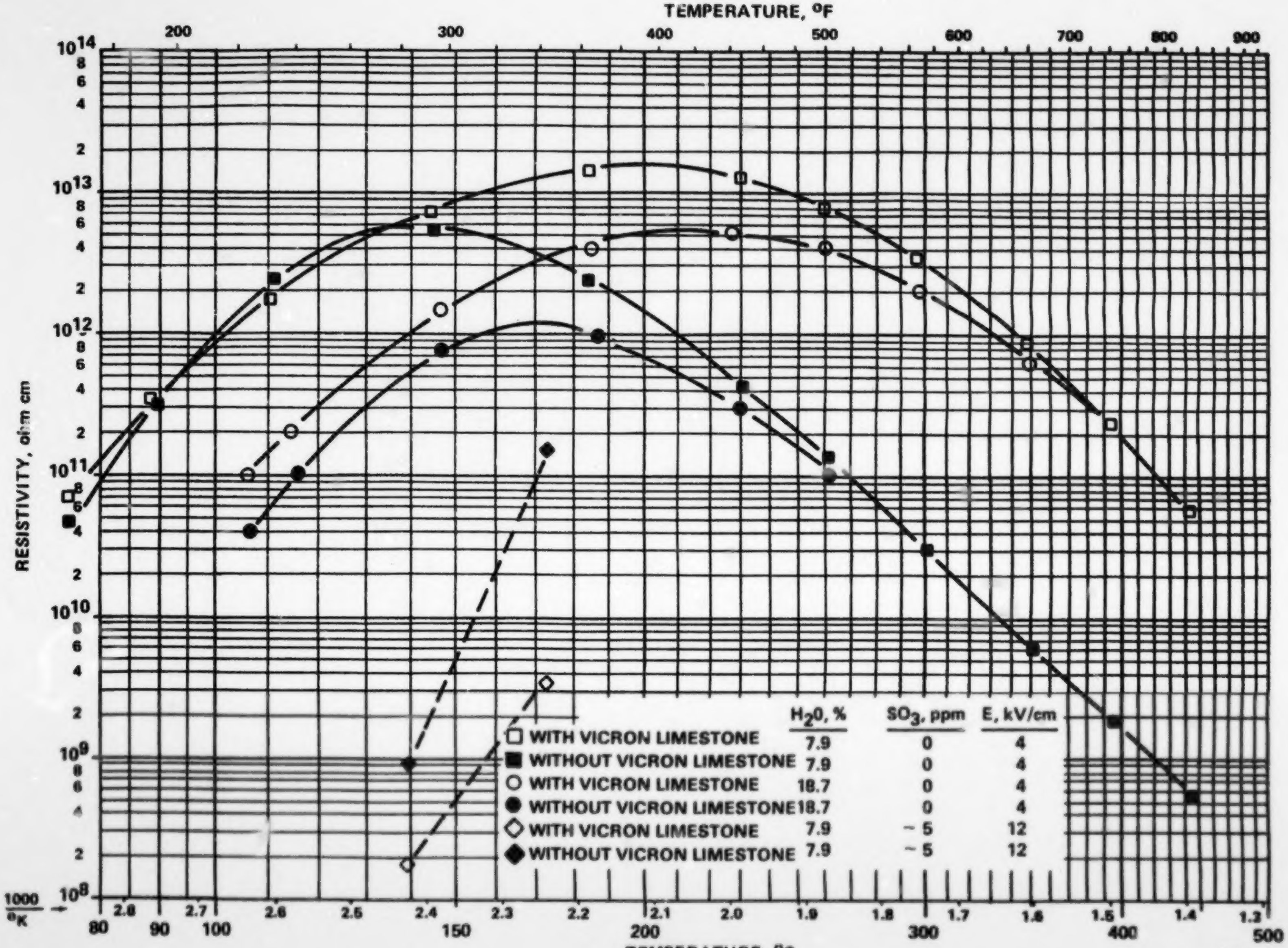
Resistivity measurements have also been made with artificially added SO_3 for conditions that result in negligible naturally occurring SO_3. These measurements indicate that resistivity attenuation can be achieved with the injection of 30 to 40 ppm of SO_3, but that the residual levels of SO_3 are sensitive to the residence time in the flue gas and the injection temperature, as well as the concentration of injected SO_3.

In situ measurements with SO_3 injection for conditioning with hydrated lime sorbent have produced ambiguous results. In situ resistivity values of 3 to 7 x 10^{11} ohm cm in the presence of 1.5 to 2 ppm of residual SO_3 have been observed at temperatures of 132 to 143°C (270 to 290°F) when hydrated lime is injected near the furnace exit. Other data indicate that resistivity values of 3 to 7 x 10^{10} ohm cm in the same temperature range are obtained in the presence of 0.5 to 1.2 ppm residual SO_3 when hydrated lime is injected nearer the flame zone. The preliminary data suggest that hydrated lime injected near the furnace exit may produce a particulate mixture difficult to condition because of the high reactivity of the unsulfated calcine which remains when the mixture reaches the resistivity port.

Effect of Sorbent Injection on Laboratory Resistivity

Laboratory resistivity measurements were performed for Indiana fly ash from furnace tests with and without Vicron limestone addition. These measurements were conducted with standard procedures developed by Bickelhaupt (14). Water vapor concentrations were varied between 7.9 and 18.7% by volume in air, and the sulfur trioxide concentration was either zero or approximately 5 ppm. For the tests involving sulfur trioxide, the ash layer and the environment were assumed to be in equilibrium when the resistivity value decreased at a rate of less than 30% in a 24-hr period. Figure 38 summarizes results obtained from these experiments. All ash samples were collected in the combustion system resistivity probe. The chemical analyses of the ash samples used in these experiments were given in Table 22. Several observations can be made from these data:

- The presence of the partially sulfated sorbent increased the response of the ash resistivity to a given SO_3 concentration. This confirms the trend shown by the in situ data in Figure 37. Five ppm of SO_3 in the environment decreased the resistivity at 149°C (300°F) by over 3 orders of magnitude.



	H_2O, %	SO_3, ppm	E, kV/cm
□ WITH VICRON LIMESTONE	7.9	0	4
■ WITHOUT VICRON LIMESTONE	7.9	0	4
○ WITH VICRON LIMESTONE	18.7	0	4
● WITHOUT VICRON LIMESTONE	18.7	0	4
◇ WITH VICRON LIMESTONE	7.9	~5	12
◆ WITHOUT VICRON LIMESTONE	7.9	~5	12

Figure 38. *Comparison of resistivities with and without Vicron limestone addition obtained with Indiana 2.3% sulfur bituminous coal.*

- The ash/sorbent mixture responds to water conditioning, but it appears that temperatures lower than 93°C (200°F) would be required to lower resistivity into the low 10^{10} ohm cm range with water vapor concentrations of 16 to 19% by volume if no SO_3 is present.

- Resistivities of ~2 x 10^{12} ohm cm are measured for ash/sorbent mixtures at hot-side ESP operating temperatures of 300°C (572°F).

Laboratory resistivity measurements were also performed with ash/sorbent mixtures produced with injection of hydrated lime downstream of the burner with the Indiana coal as fuel. Results from these experiments were similar to those shown in Figure 38.

Effect of Sorbent Injection on Particle Size Distribution

An electrical aerosol size analyzer (EASA) and an optical particle counter (OPC) were used to measure the particle size distributions of fly ash and fly ash/sorbent mixtures suspended in the flue gas at the resistivity port, where the gas temperature was about 149°C (300°F). These data were obtained while the Indiana Batch No. 2 coal was being fired at full load (36.3 kg/hr [80 lb/hr] or 1.06 GJ/hr [1 x 10^6 Btu/hr]). The combustor was coaxially staged with the burner and tertiary air flows representing 76 and 48%, respectively, of the stoichiometric air requirement. Four different conditions were investigated:

(1) A baseline condition with no sorbent injection,

(2) Vicron limestone added at the burner at a rate of 4.63 kg/hr (10.19 lb/hr) (CaS ~1.9),

(3) Vicron limestone added at S-4 at the same rate, and

(4) Longview hydrated lime added at S-4 at a rate of 3.42 kg/hr (7.54 lb/hr) to produce the same Ca/S ratio.

With the Vicron limestone addition at the burner and at S-4, the SO_2 removals after 10 min were 35 and 40%, respectively. With the Longview hydrated lime added at S-4, the removal after 10 min was about 45%.

Effect of Burner Injection of Vicron Limestone--

Figure 39 shows the effect of burner injection of Vicron 45-3 limestone on the particle size distribution. The data show a marked increase in the mass concentration in the size range of about 0.1 to 0.8 µm. Since cascade impactors were not run, no size data were obtained above 0.8 µm. The ultrafine data are sufficient, however, to demonstrate a potential fine particle problem with burner injection of the sorbent. These fine particles could have serious implications on ESP performance and stack opacity.

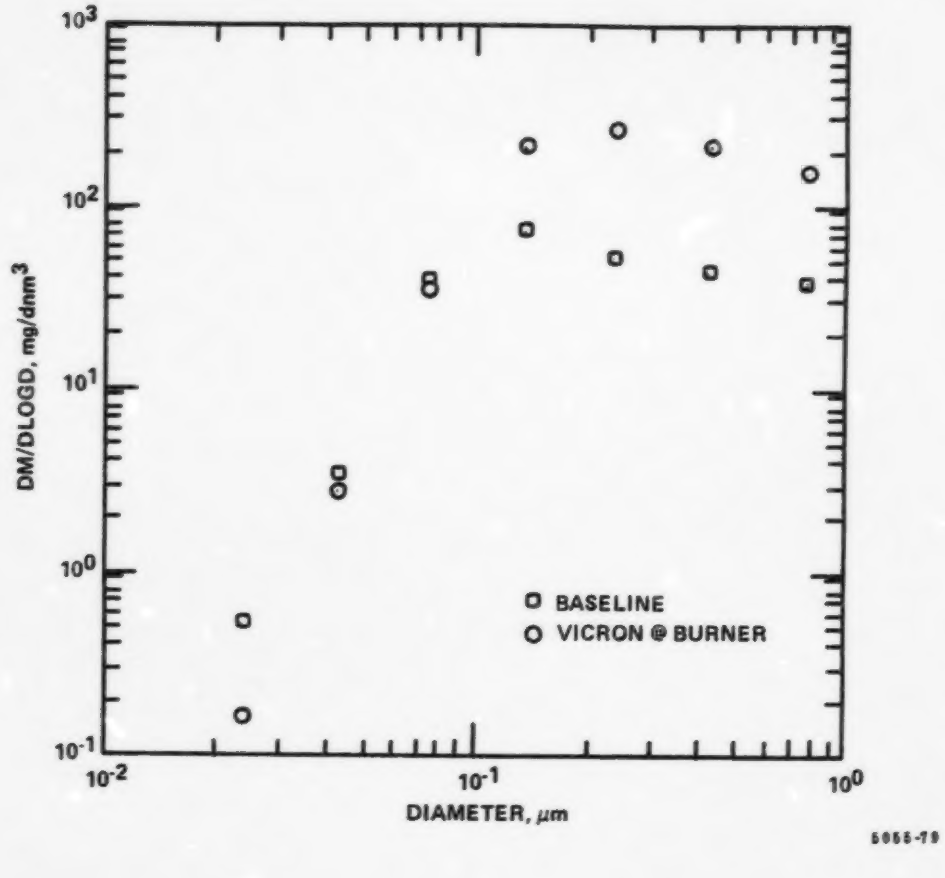


Figure 39. Effect of burner injection of Vicron limestone on the particle size distribution obtained with Indiana Lot No. 2 coal.

Effect of S-4 Injection of Vicron Limestone--

Figure 40 shows the effect of Vicron limestone injection at S-4 on the particle size distribution, in comparison to the effect observed with burner injection. Clearly, injection at S-4 produces fewer fine particles in the size range of 0.1 to 0.8 µm. This suggests that the ESP problems associated with fine particles may be partially alleviated by injection of the sorbent at some point downstream from the burner. Presumably, the lower gas temperatures result in less decrepitation of the sorbent.

Comparison of Vicron Limestone and Longview Hydrated Lime Injected at S-4--

Figure 41 shows a comparison between the injection of Vicron limestone and Longview hydrated lime at S-4. The data indicate no difference in the two particle size distributions over the range of particle sizes resolved by the EASA and OPC. However, there may be major differences at particle sizes above 0.8 µm. This is suggested because the Longview hydrated lime is known to be much finer than the Vicron limestone. In the ultrafine range, however, there appears to be little difference.

Effect of SO_3 Conditioning with Sorbent Injection

SO_3 Conditioning Trials with Indiana Coal and Vicron Limestone--

These tests were done with Vicron limestone added at the burner and the SO_3 injection at a point about 29.6 m (97 ft) ahead of the resistivity port, where the gas temperature was 571°C (1060°F). This injection point may not be realistic in terms of the temperature, but it provided a reasonable SO_3-particulate contact time of about 1.3 sec.

In these tests, the second batch of Indiana coal was fired at a rate of 1.06 GJ/hr (1 x 10^6 Btu/hr) with 65% of the stoichiometric air requirement supplied at the burner and 55% supplied through the tertiary ports. The Vicron limestone was injected through the burner core at a rate sufficient to produce a Ca/S mole ratio of 1.78:1. Under these conditions, the gas-phase SO_2 capture was estimated to be 20 to 21%.

The results of the conditioning tests with Indiana coal and Vicron limestone are tabulated in Table 23 and plotted in Figure 42. These data show that an ash/sorbent mixture having an initial resistivity of about 1.5 x 10^{12} ohm cm can be conditioned to a resistivity level below 5 x 10^{10} ohm cm by the injection of about 38 ppm SO_3, and this can be accomplished within a reasonable contact time. However, under these conditions a considerable amount of SO_3 (~15 ppm) is left in the gas phase. The residual level of SO_3 may be lower, however, if the contact time is provided in an essentially isothermal duct at 149°C (300°F) rather than in a system where the gas is cooling down from 571°C (1060°F) to 149°C (300°F). With the SRI coal combustion facility in its original configuration, a comparable length of isothermal contact time at 149°C (300°F) was not feasible. Therefore, it was decided to construct a well-insulated chamber in which isothermal residence times on the order of 1 sec could be achieved. This provided a more realistic simulation of the flue gas flowing from the air heater to the ESP in an actual plant. This configuration was used in all subsequent tests of SO_3 conditioning.

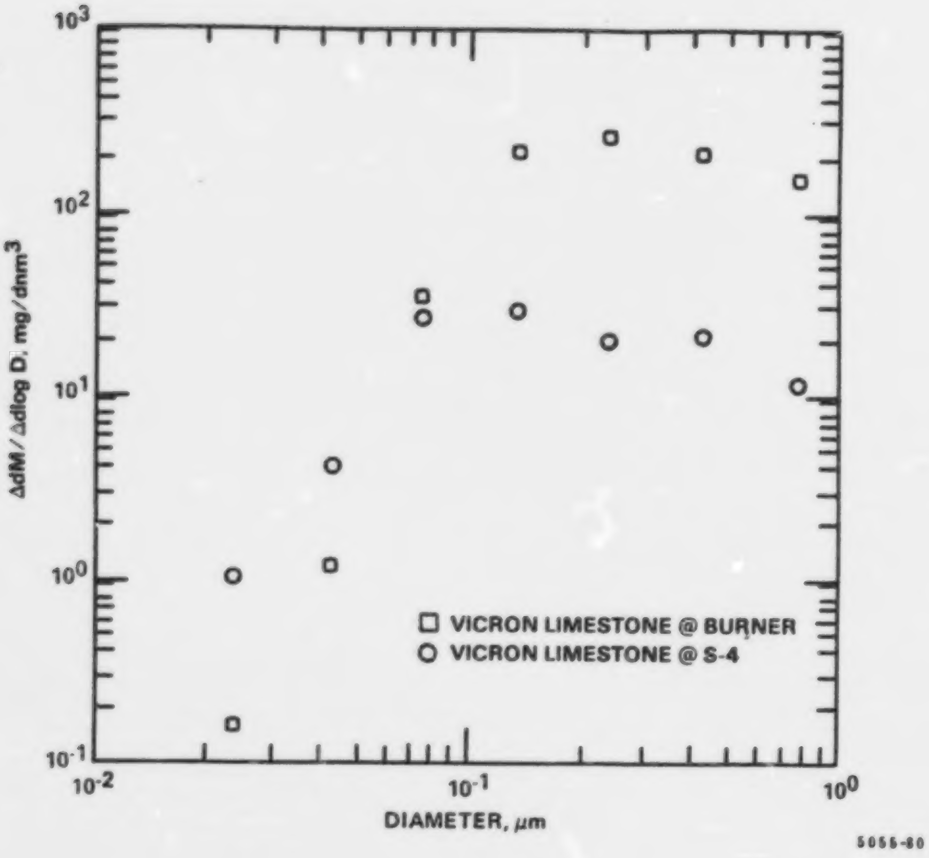


Figure 40. Effect of Vicron limestone injection at S-4 on the particle size distribution compared to the effect of burner injection.

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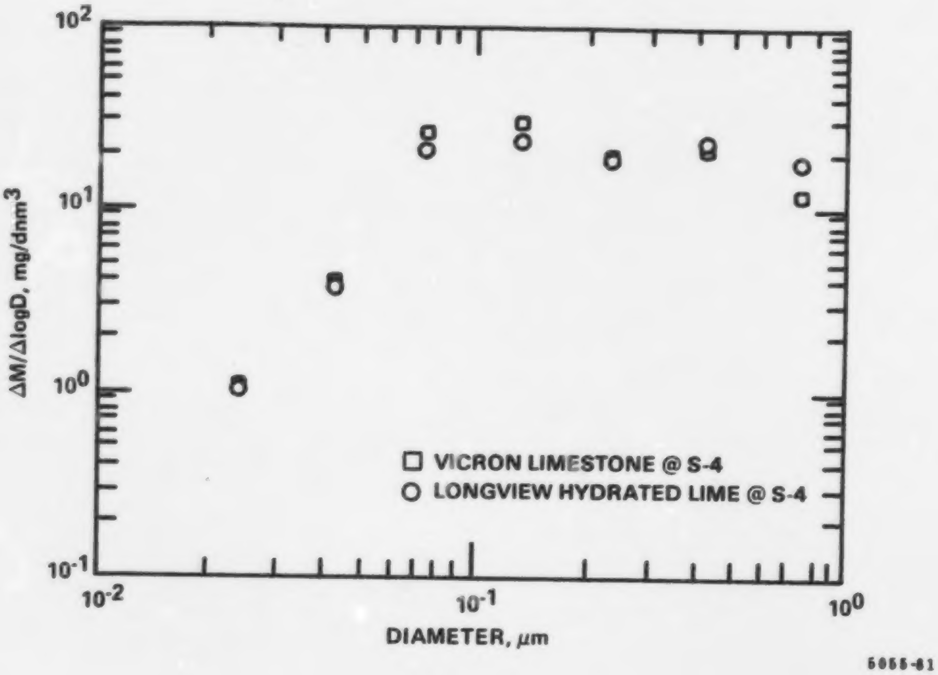


Figure 41. Comparison of particle size distributions obtained with Vicron limestone and Longview hydrated lime injected at S-4.

TABLE 23. RESULTS OF SO_3 CONDITIONING TRIALS WITH INDIANA LOT NO. 2 COAL AND VICRON LIMESTONE

Run No. (C280-1	SO_3 injection rate[a] (ppm)	Sorbent addition rate (Ca/S)	Measured SO_3 (ppm)	Flue gas temp (°C [°F])	In situ (spark) resistivity (ohm cm)
51-2	0	0	2.5	146 [294]	1.8×10^{11}
51-3	0	0	2.7	151 [304]	2.6×10^{11}
51-5	0	0	ND[b]	149 [300]	4.0×10^{11}
51-7	0	1.8	nil[c]	150 [302]	1.2×10^{12}
51-8	0	1.8	nil	153 [307]	2.1×10^{12}
51-9	0	1.8	nil	158 [317]	1.1×10^{12}
60-1	67	1.8	ND	156 [312]	1.9×10^{9}
60-2	67	1.8	ND	152 [306]	4.2×10^{8}
60-3	67	1.8	ND	153 [307]	1.5×10^{8}
60-4	67	1.8	39	157 [314]	1.7×10^{9}
60-5	67	1.8	39	158 [317]	3.6×10^{9}
60-6	38	1.8	18	157 [314]	1.2×10^{10}
60-7	38	1.8	14	156 [312]	7.7×10^{10}

a. Theoretical SO_3 injection rate corrected for wall losses

b. ND - not determined

c. <0.2 ppm

CONDITIONS:
Fuel = Indiana Lot No. 2 coal
Load = 1.06 GJ/hr (1 x 10^6 Btu/hr)
$SR_B \cong 65\%$
$SR_O = 120\%$
Sorbent = Vicron limestone
Sorbent injection rate = 4.567 kg/hr (10.06 lb/hr) = 0.761 gmole/min
SO_2 measured at return bend without sorbent = 1800 ppm = 0.428 gmole/min
Ca/S = 0.761/0.428 = 1.78
SO_2 measured at return bend with sorbent = 1430 ppm (instantaneous)
1300 ppm (long-term)
Gas-phase removal = 20.6%
Temperature at SO_3 injection point ≅ 571°C (1060°F)
Residence time between injection point and resistivity port = 1.3 sec

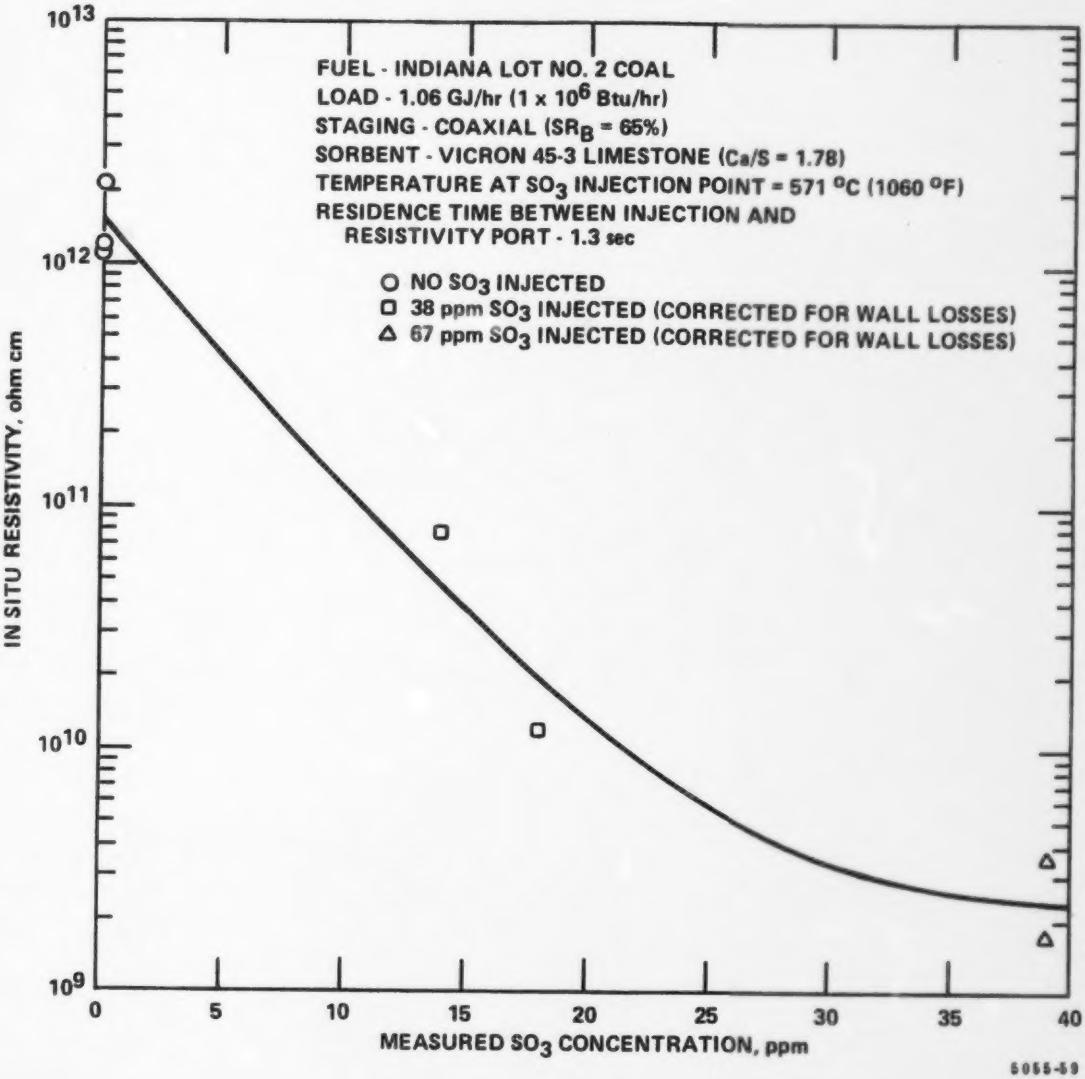


Figure 42. Effect of SO_3 conditioning on the resistivity of Indiana fly ash/sorbent mixture. (Note that residual SO_3 levels are too high due to inadequate contact time at cold-side temperatures; this is being corrected by the installation of an "isothermal" residence chamber).

It appears that SO_3 conditioning can provide a solution to the resistivity problem associated with the LIMB process (at least, with this specific ash-sorbent combination). However, the conditioning process must be "tuned" to minimize residual SO_3 levels while producing the desired resistivity attenuation.

Effect of Sorbent Injection Location on SO_3 Conditioning--

In situ measurements--A modified point-plane probe was used to make in situ resistivity measurements with and without the injection of Longview hydrated lime at S-3, S-4, and the burner. The results of these measurements are summarized in Table 24 and Figures 43 and 44. All of these data were obtained at the resistivity port where the flue gas temperature was 121 to 132°C (250 to 270°F), except as noted in the table. Batch No. 3 of the Indiana coal (~2.6% sulfur) was the fuel used during these tests.

The residual SO_3 levels given in Table 24 and Figure 44 should be viewed with caution. These measured SO_3 levels may be too low due to loss of SO_3 to the unreacted sorbent collected on the quartz wool plug ahead of the controlled condensation apparatus. The quartz wool plug is maintained at a temperature of 274°C (525°F), which is sufficient to prevent the uptake of SO_2. However, SO_3 is more reactive than SO_2 at this temperature. A modified procedure for sampling SO_3 in the presence of reactive sorbents is currently being developed under EPA Cooperative Agreement No. CR812222, "Analytical Support for LIMB Development."

In the absence of any SO_3 conditioning, both S-3 and S-4 injection of the hydrated lime produced a high resistivity ash (~8-9 x 10^{11} ohm cm). However, the S-3 ash could be conditioned with SO_3 while the S-4 ash could not, as shown in Figure 38. With S-3 injection, the ash resistivity was reduced to 3 x 10^{11} ohm cm with 45 ppm of SO_3 added to the flue gas, and to 9 x 10^9 ohm cm with 115 ppm of SO_3 injected. With S-4 injection, however, the resistivity remained high even at the 115 ppm level of injection.

The effect of the injection location on the ability to condition the ash may be explained in terms of the sorbent utilization. The higher degree of utilization obtained at S-3 would be expected to produce a more highly sulfated material that would be more amenable to conditioning without excessive uptake of SO_3. In contrast, the S-4 ash would contain more unused, reactive sorbent which may tend to absorb large quantities of SO_3 without producing the desired conditioning effect on the particulate surface.

The explanation offered above may appear to be inconsistent with the results obtained with burner injection, where the utilization is relatively low but the ash has a low resistivity even without added SO_3. However, if the sorbent is sintered during burner injection, the interior of the sorbent particles may not be accessible. The SO_3 would then be confined to the surface, and it may be possible to obtain the desired conditioning effect with only the naturally occurring SO_3.

TABLE 24. IN SITU RESISTIVITY DATA OBTAINED WITH LONGVIEW HYDRATED LIME AND INDIANA COAL

Sorbent injection site	Calcium-to-sulfur ratio	Sulfur capture (%)	SO_3 added (ppm)	Residual SO_3 (ppm)	Number of resistivity runs	In situ resistivity (ohm cm) Mean	Standard deviation	Gas temp (°C [°F])
S-4	1.47	40.6	0	<0.3	3	8.75×10^{11}	3.45×10^{11}	129 [264]
S-4	1.425	40.1	45	<0.3	4	1.34×10^{12}	1.13×10^{12}	129 [265]
S-4	1.49	42.1	115	<0.3	5	4.88×10^{11}	2.05×10^{11}	133 [272]
S-3	1.49	57.2	0	<0.3	3	8.32×10^{11}	1.22×10^{12}	152 [306][a]
S-3	1.70	56.5	45	0.6	5	2.77×10^{11}	1.90×10^{11}	126 [258]
S-3	1.65	55.9	115	7.5	4	9.31×10^{9}	2.67×10^{9}	127 [260]
B	1.61	37.6	0	3.5	3	1.38×10^{9}	9.28×10^{8}	126 [258]
(--)[b]	0	—	--	14.5	2	3.70×10^{8}	—	127 [260]

a. Flue gas temperature varied from 138 to 181°C (280 to 357°F) during these runs.

b. Baseline coal only; no sorbent injected.

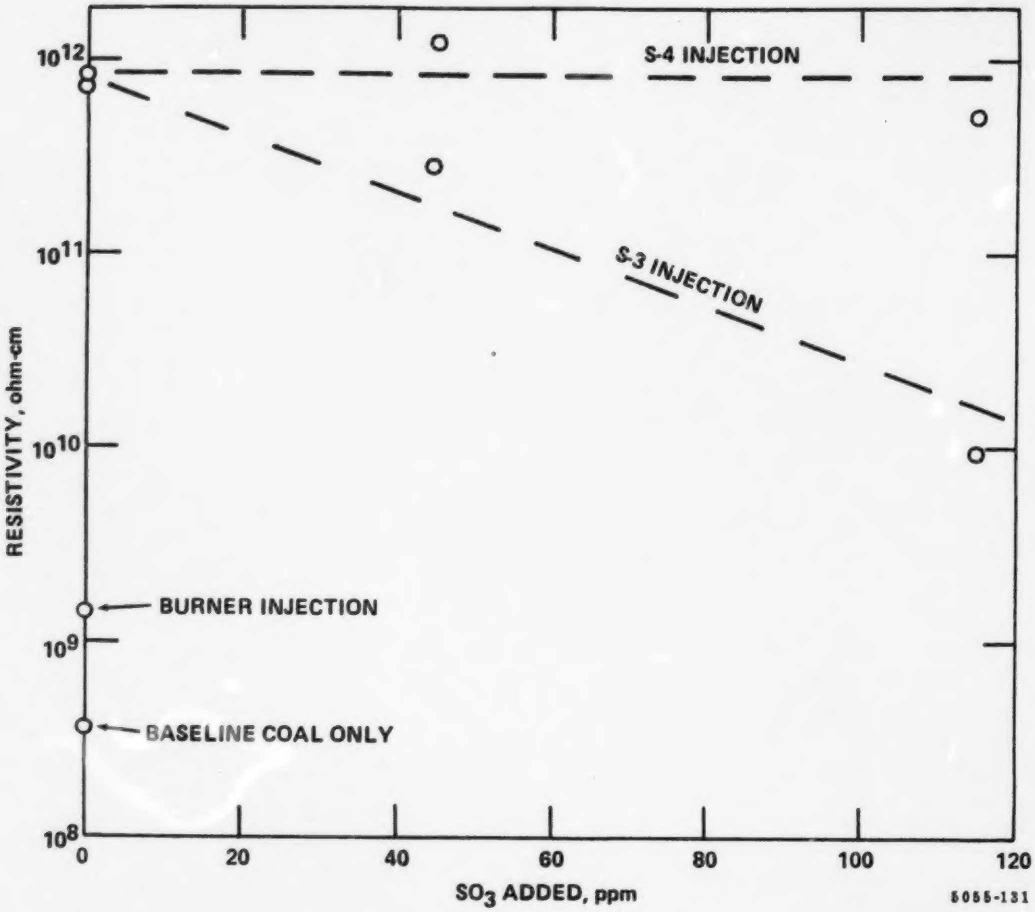


Figure 43. In situ resistivity measurements with Longview hydrated lime injection and SO_3 conditioning.

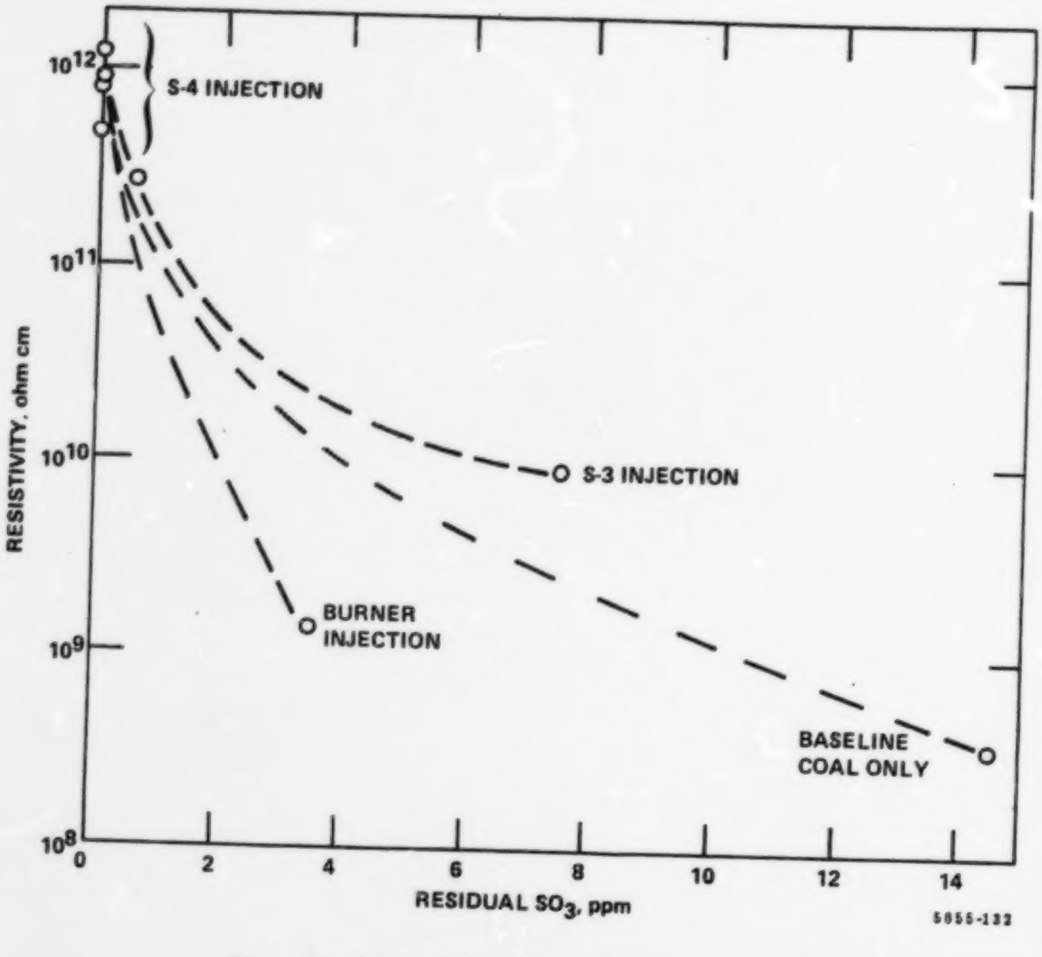


Figure 44. In situ resistivity as a function of residual SO_3.

Laboratory studies--The results of laboratory measurements on fly ash produced by burning Indiana Batch No. 3 coal with and without the injection of hydrated lime in the SRI coal combustor are shown in Figures 45 and 46. Both Longview test samples are composites of three samples collected in the cavity of the in situ resistivity probe, one set collected with coal only and one set collected with Longview hydrated lime injected at S-4. The latter composite represents the samples that could not be conditioned in the in situ tests.

Note that there is a two order of magnitude difference in the resistivity scales of the two plots with the sample with injection of hydrated lime producing the higher resistivity. The test environment contained a nominal 8% water vapor (by volume) for all tests and the amount of SO_3 was varied from 0 to 11 ppm. The actual measured concentration is indicated in the box on each plot. The resistivity data, when no SO_3 was in the test atmosphere, were obtained according to IEEE Standard 548-1981, descending temperature technique. When SO_3 was present in the test environment, the general procedure described by Bickelhaupt (14) was used to obtain resistivity values at temperatures of about 160 and 135°C (320 and 275°F), using fresh samples for each level of SO_3 tested. For these tests, when the resistivity value decreased at a rate of less than 30% in a 24-hr period, the ash layer and environment were assumed to be in equilibrium.

A comparison of Figures 45 and 46 shows that adding SO_3 to the test environment is even more effective at lowering the resistivity of the ash/sorbent mixture than for the ash alone. In fact, at the temperatures tested, nominally equal concentrations of SO_3 result in resistivities of the ash/sorbent mixture which are equal to or less than the corresponding resistivities for the ash alone. This is found even though the peak resistivities differ by an order of magnitude when no SO_3 is present. Therefore, the laboratory tests suggest that this ash should respond readily to SO_3 conditioning, even though it showed no response in the in situ tests. This may suggest that the time required for equilibration is longer than the residence time available in the combustor.

An attempt was made to predict the laboratory resistivity of the two samples using Model II of the resistivity prediction program developed by Bickelhaupt (23). The results are shown in Figures 47 and 48 for the ash only and for the ash/sorbent mixtures, respectively. For simplicity, only the laboratory measurements at the two extremes of SO_3 concentration are superimposed on the computer predictions. In addition, it should be noted that for the case when no SO_3 was present in the test atmosphere a general agreement between measured and predicted values was obtained for both samples.

As expected, Figure 47 shows that the predicted values of resistivity when SO_3 is present agree quite well with the measured values for the case where there was no injection of hydrated lime. However, Figure 48 reveals a large discrepancy between measured and predicted resistivity values for the case of injection of the hydrated lime. The computer program predicts values of resistivity roughly one order of magnitude higher than what was actually measured in the laboratory. Thus, it appears that the computer program for predicting

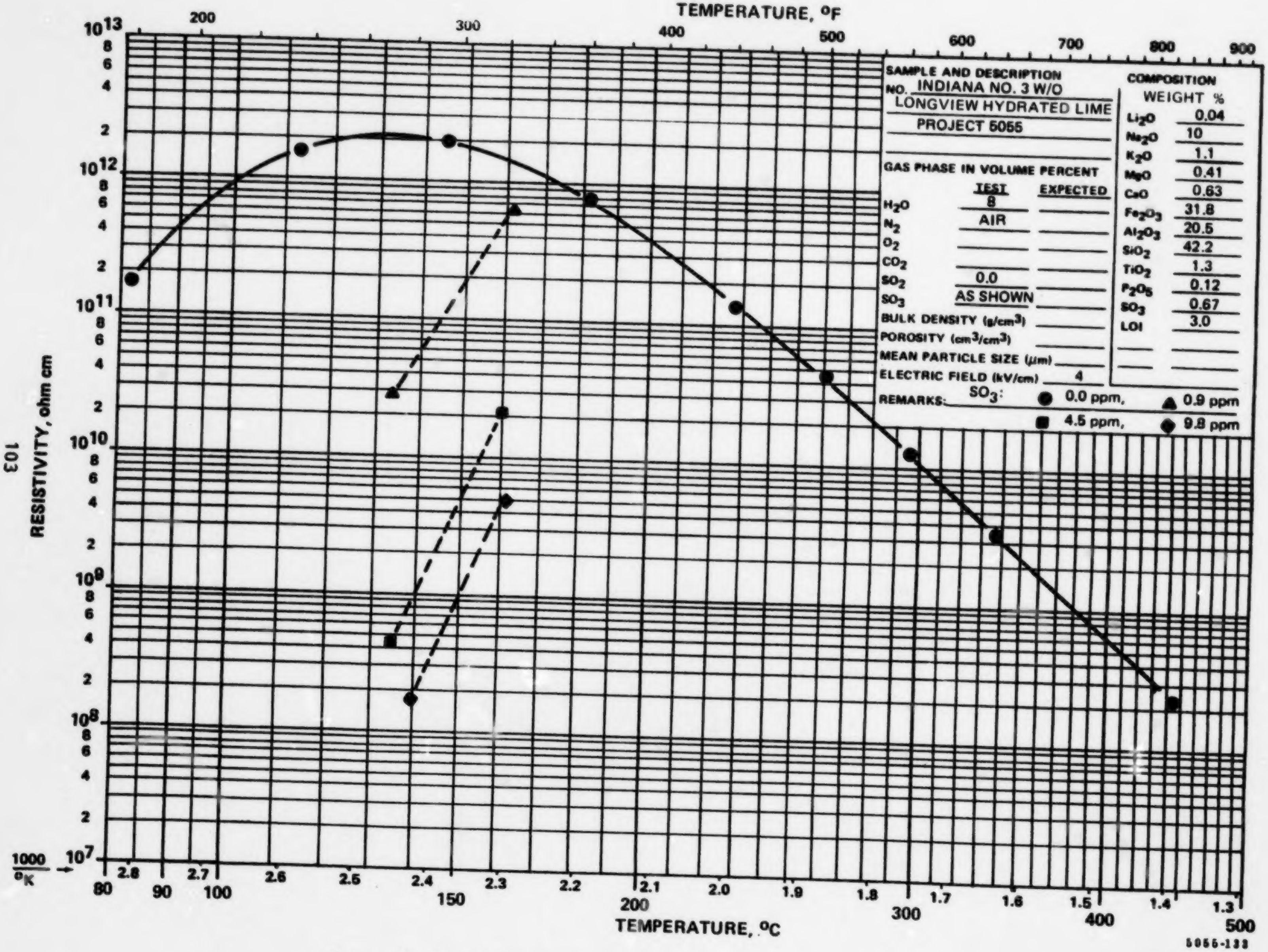
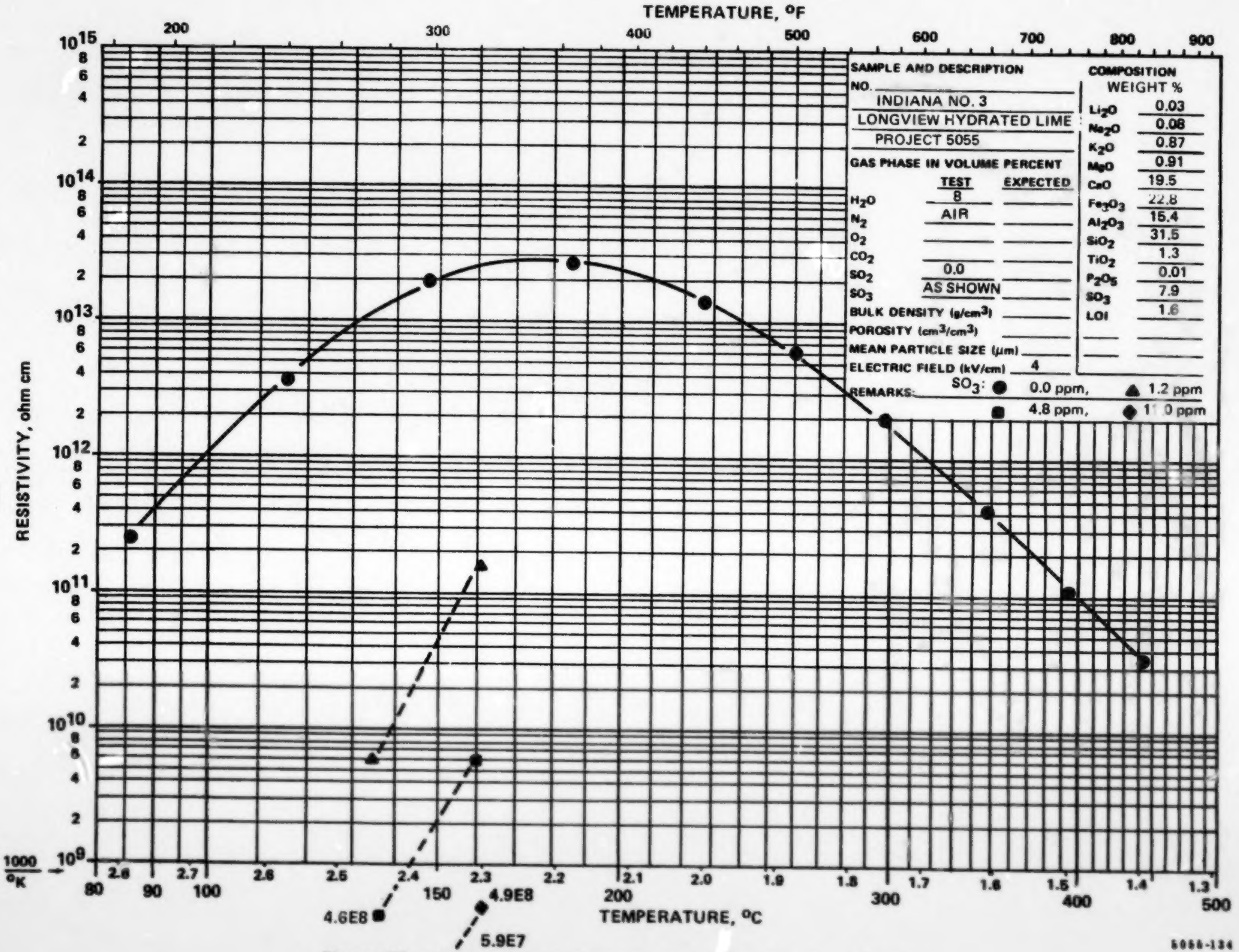


Figure 45. Laboratory resistivity data for Indiana fly ash without sorbent.



SAMPLE AND DESCRIPTION

NO. INDIANA NO. 3

LONGVIEW HYDRATED LIME

PROJECT 5055

GAS PHASE IN VOLUME PERCENT

	TEST	EXPECTED
H_2O	8	
N_2	AIR	
O_2		
CO_2		
SO_2	0.0	
SO_3	AS SHOWN	

BULK DENSITY (g/cm^3)

POROSITY (cm^3/cm^3)

MEAN PARTICLE SIZE (μm)

ELECTRIC FIELD (kV/cm) 4

REMARKS: SO_3: ● 0.0 ppm, ▲ 1.2 ppm, ■ 4.8 ppm, ◆ 11.0 ppm

COMPOSITION WEIGHT %

Li_2O	0.03
Na_2O	0.08
K_2O	0.87
MgO	0.91
CaO	19.5
Fe_2O_3	22.8
Al_2O_3	15.4
SiO_2	31.5
TiO_2	1.3
P_2O_5	0.01
SO_3	7.9
LOI	1.6

Figure 46. Laboratory resistivity data for Indiana fly ash with sorbent.

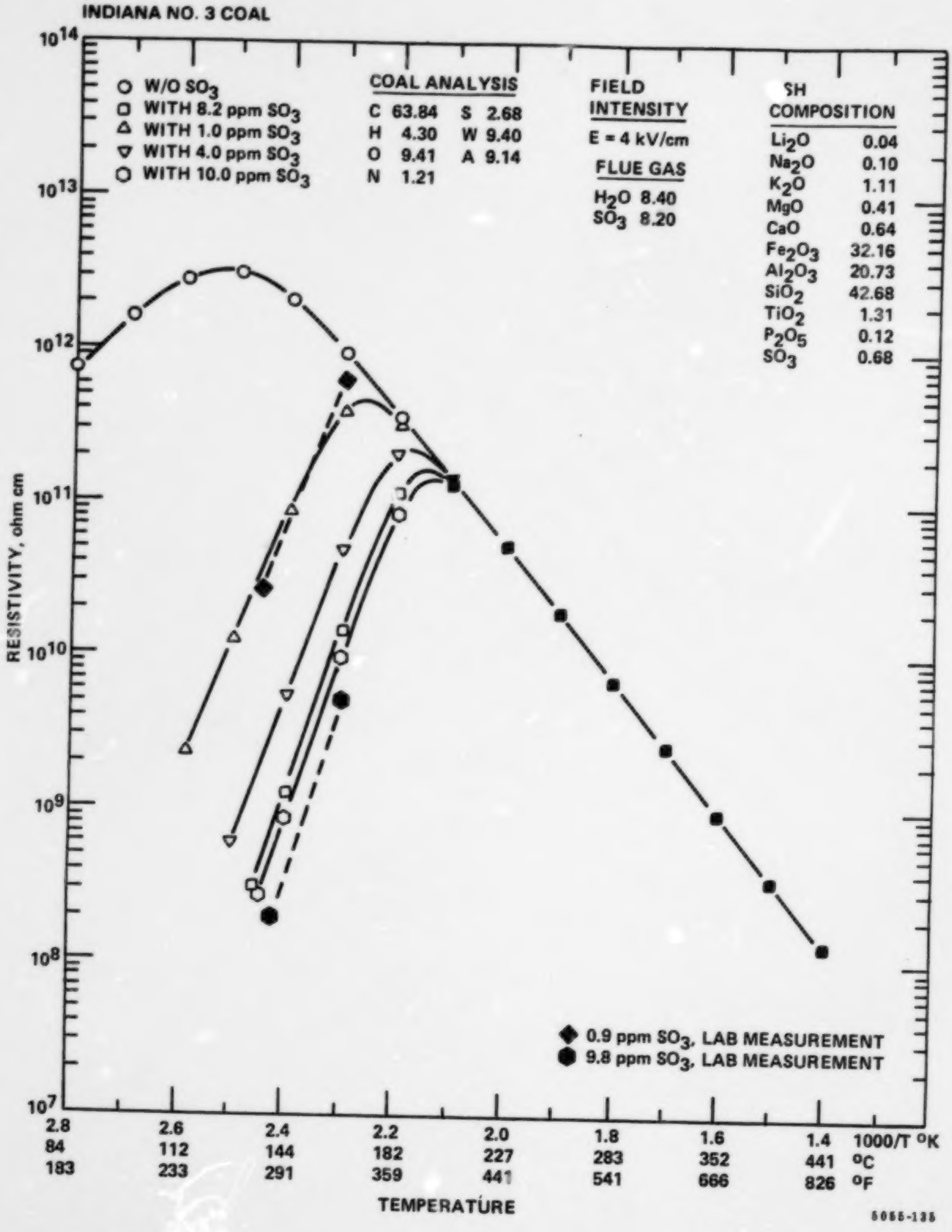


Figure 47. Predicted resistivity values for Indiana fly ash at various SO_3 levels compared to laboratory data.

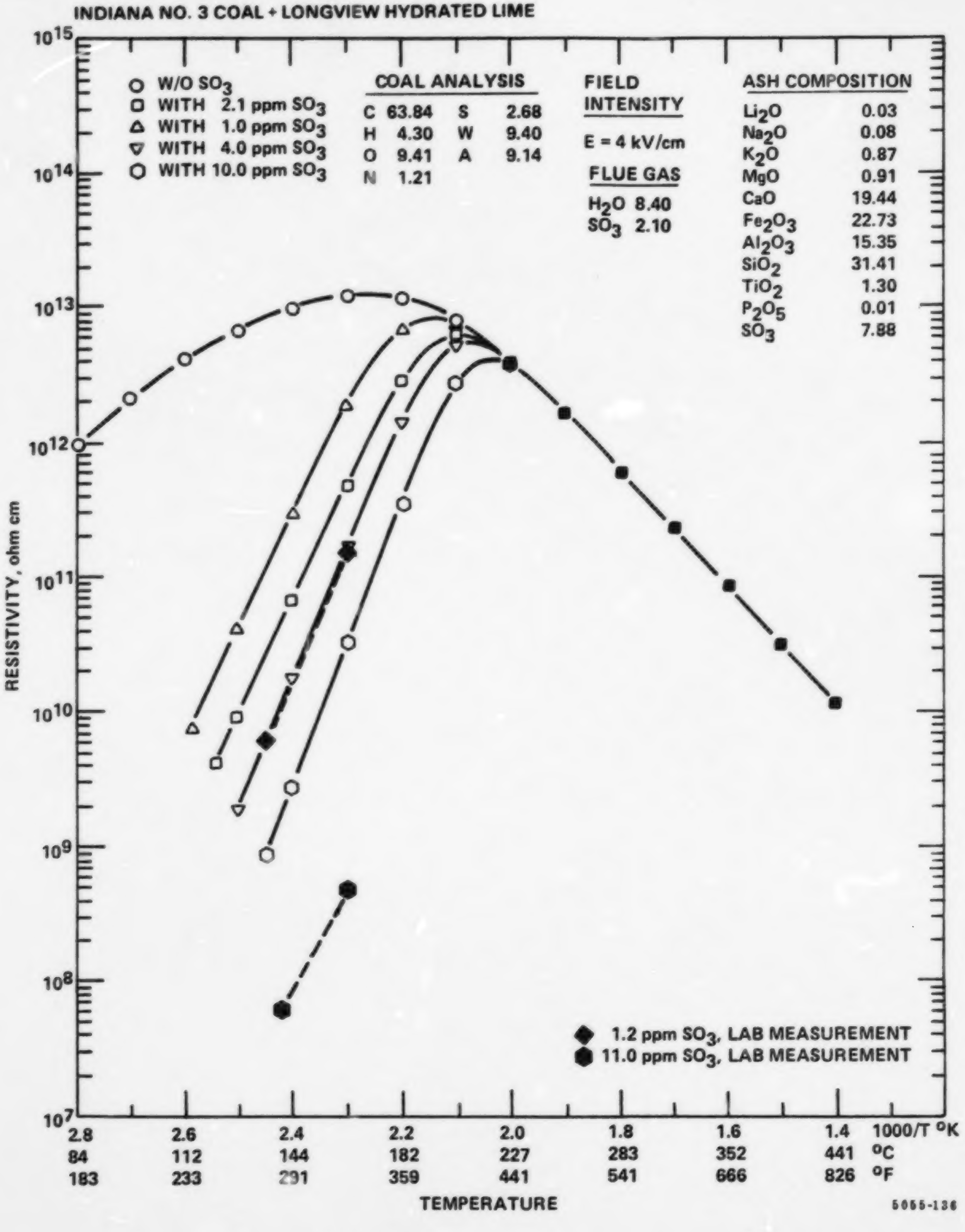


Figure 48. Predicted resistivity values for ash/sorbent mixture at various SO_3 levels compared to laboratory data.

resistivity cannot be used in its present form when hydrated lime is injected into the furnace and SO_3 is present in the flue gas in significant amounts.

PREDICTED EFFECT OF SORBENT INJECTION ON ESP PERFORMANCE

Since downstream injection of sorbent generally produces superior SO_2 capture compared to burner injection, without the problem of excessive fine particle production, this mode of sorbent injection was chosen for precipitator performance simulations using the EPA/SRI model of electrostatic precipitation (25). The model simulations were performed to evaluate the effects of sorbent addition on ESP performance. The potential effects of ESP design modification and SO_3 conditioning for counteracting the effects of sorbent injection were also investigated. A particle size distribution was constructed from impactor and ultrafine data with downstream injection of Vicron limestone. The baseline and with-sorbent distributions are presented in Figure 49, on a basis of cumulative mass per unit volume of gas as a function of particle diameter. Electrical data for the simulations were based on the following assumptions:

- The fly ash resistivity without sorbent was 2×10^{10} ohm cm.
- Vicron addition produced 2×10^{12} ohm cm dust without conditioning.
- SO_3 conditioning restored resistivity of the ash/sorbent mixture to 2×10^{10} ohm cm.

The objective of these simulations was to examine the predicted precipitator performance for existing and modified precipitators in a specific collection area range likely to be encountered in a retrofit application of LIMB technology. Electrode modifications were simulated which consisted of adding a precharging section with conventional electrode geometry, followed by three collecting sections with 0.95-cm (3/8-in.) diameter wires with 22.9-cm (9-in.) plate spacing. These modifications are intended to increase the collection efficiency within the constraints imposed by the existing precipitator installation. The ESP mechanical parameters are provided in Table 25, and the electrical parameters are summarized in Table 26. The parameters assumed for the retrofit electrode modifications are given in Table 27. The particle charge values calculated for the precharger exit are similar to those expected at the exit of a cold-pipe precharger, which has been developed by Denver Research Institute (26).

Figure 50 presents the results of the simulations of collection efficiency for the indicated cases, and Figure 51 provides the ESP performance in terms of nanograms of outlet mass loading per Joule, or pounds of outlet mass loading per 10^6 Btu. These graphs show that, as expected, the high resistivity and increased mass loading associated with LIMB sorbent addition produce unacceptably high emissions. If electrical conditions are restored by SO_3 conditioning, the precipitator collection efficiency is increased over the baseline case (as a result of space charge and the higher concentration of larger particles resulting from sorbent injection), but the outlet emissions are still

2

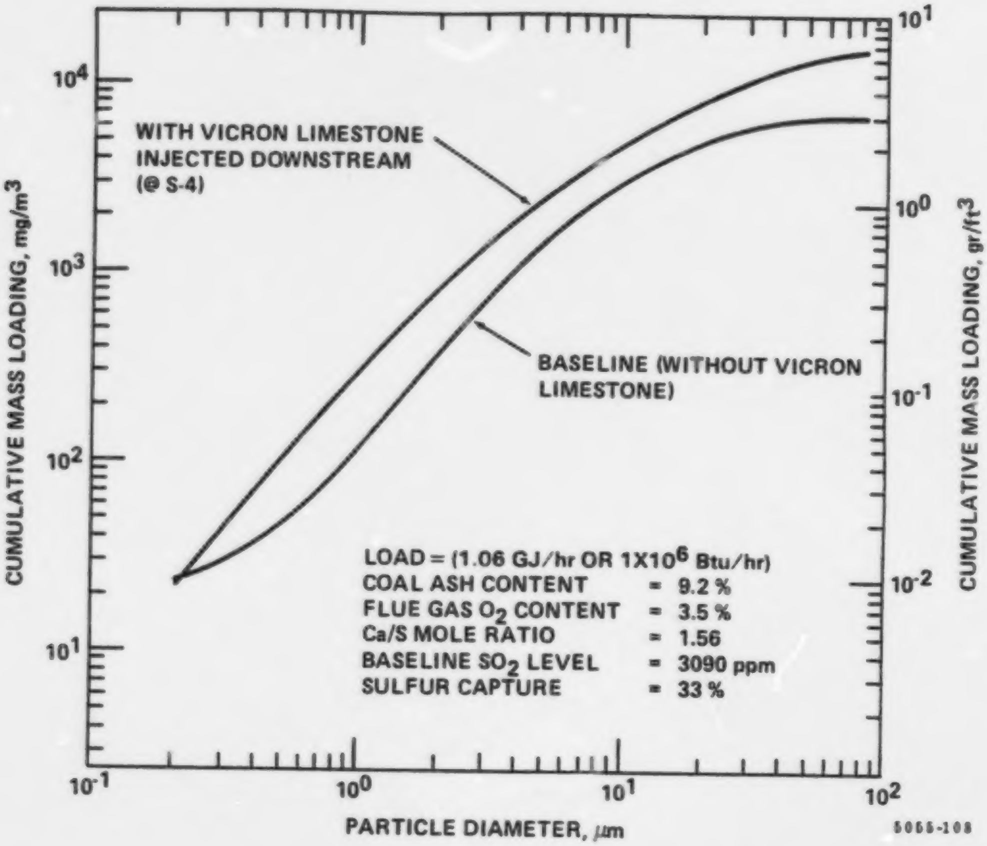


Figure 49. Comparison of cumulative mass loading curves for Indiana fly ash with and without Vicron limestone added downstream.

TABLE 25. PRECIPITATOR MECHANICAL PARAMETERS

Three electrical sections in the direction of gas flow
Three baffled sections in the direction of gas flow
Gas sneakage per baffled section = 10%
Weighted wires in 22.9-cm (9-in.) ducts
Mean gas velocity = 1.52 m/sec (5.0 ft/sec)
Relative standard deviation of mean gas velocity = 0.25
Gas flow rate = 165 m^3/sec (350,000 ft^3/min)
Plate area per section = 2,434 m^2 (26,200 ft^2)
Specific collection area = 44.3 m^2/m^3/sec (225 ft^2/1000 ft^3/min)

TABLE 26. PRECIPITATOR ELECTRICAL PARAMETERS

- High-sulfur bituminous coal
  Ash resistivity = 2 x 10^{10} ohm cm at 149°C (300°F)

Section	kV	nA/cm^2
1	43	20
2	42	29
3	40	30

- Coal and limestone
  Ash resistivity = 2 x 10^{12} ohm cm at 149°C (300°F)

Section	kV	nA/cm^2
1	30	0.8
2	29	1.2
3	30	2.5

- Coal and limestone, with SO_3 conditioning
  Ash resistivity = 2 x 10^{10} ohm cm at 149°C (300°F)

TABLE 27. PRECIPITATOR RETROFIT PARAMETERS

- Flue gas conditioning with SO_3
  Ash resistivity = 2×10^{10} ohm cm at 149°C (300°F)
- One precharging section, 0.61 m (2 ft) long,
  with 0.254-cm (0.1-in.) wires in 22.9-cm (9-in.) ducts
  Precharging section: 45 kV, and 50 nA/cm^2
- Three collection sections,
  with 0.95-cm (3/8-in.) wires in 22.9-cm (9-in.) ducts
  Each section: 50 kV, and 10 nA/cm^2

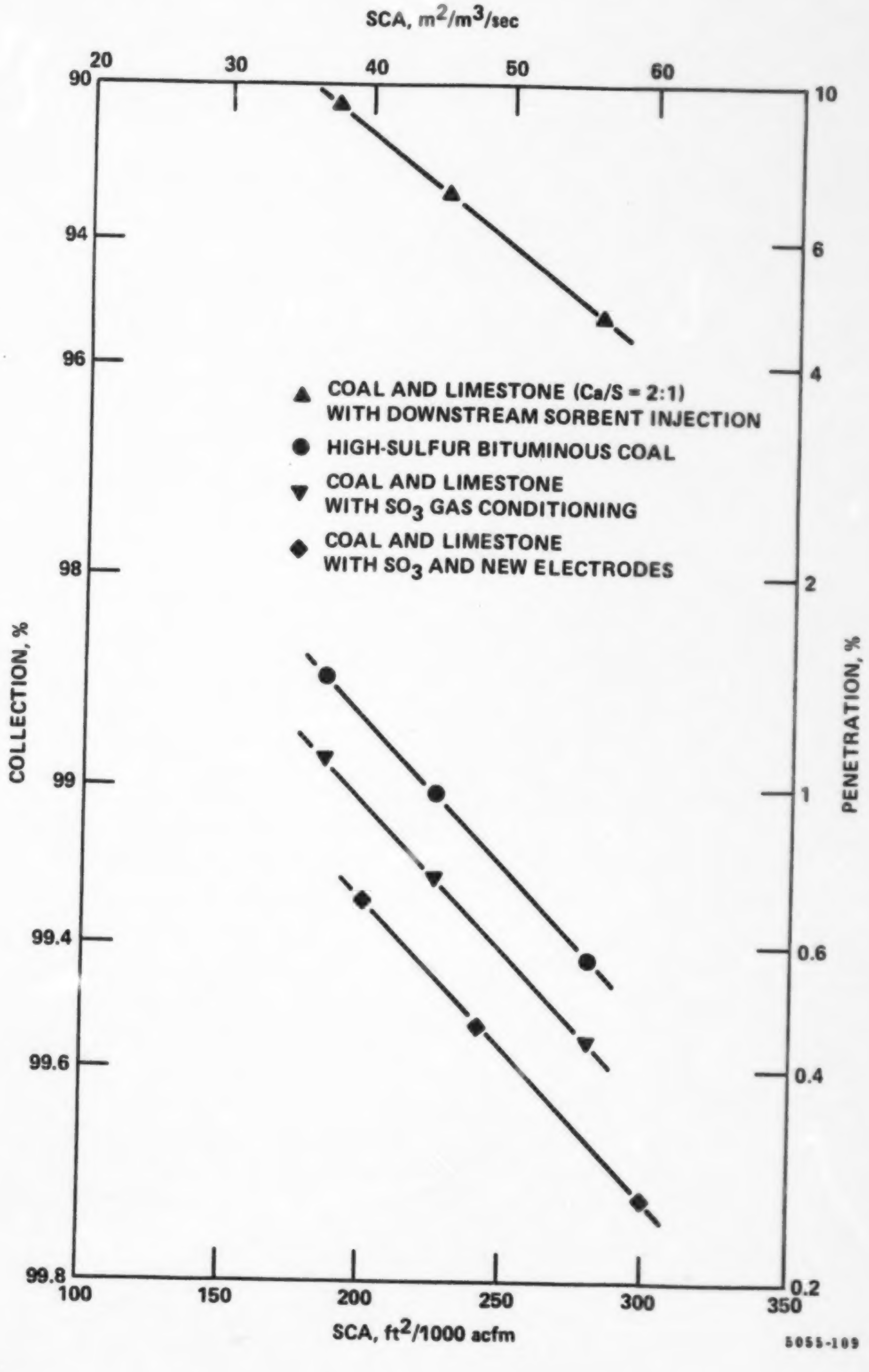


Figure 50. Results from ESP model simulation.

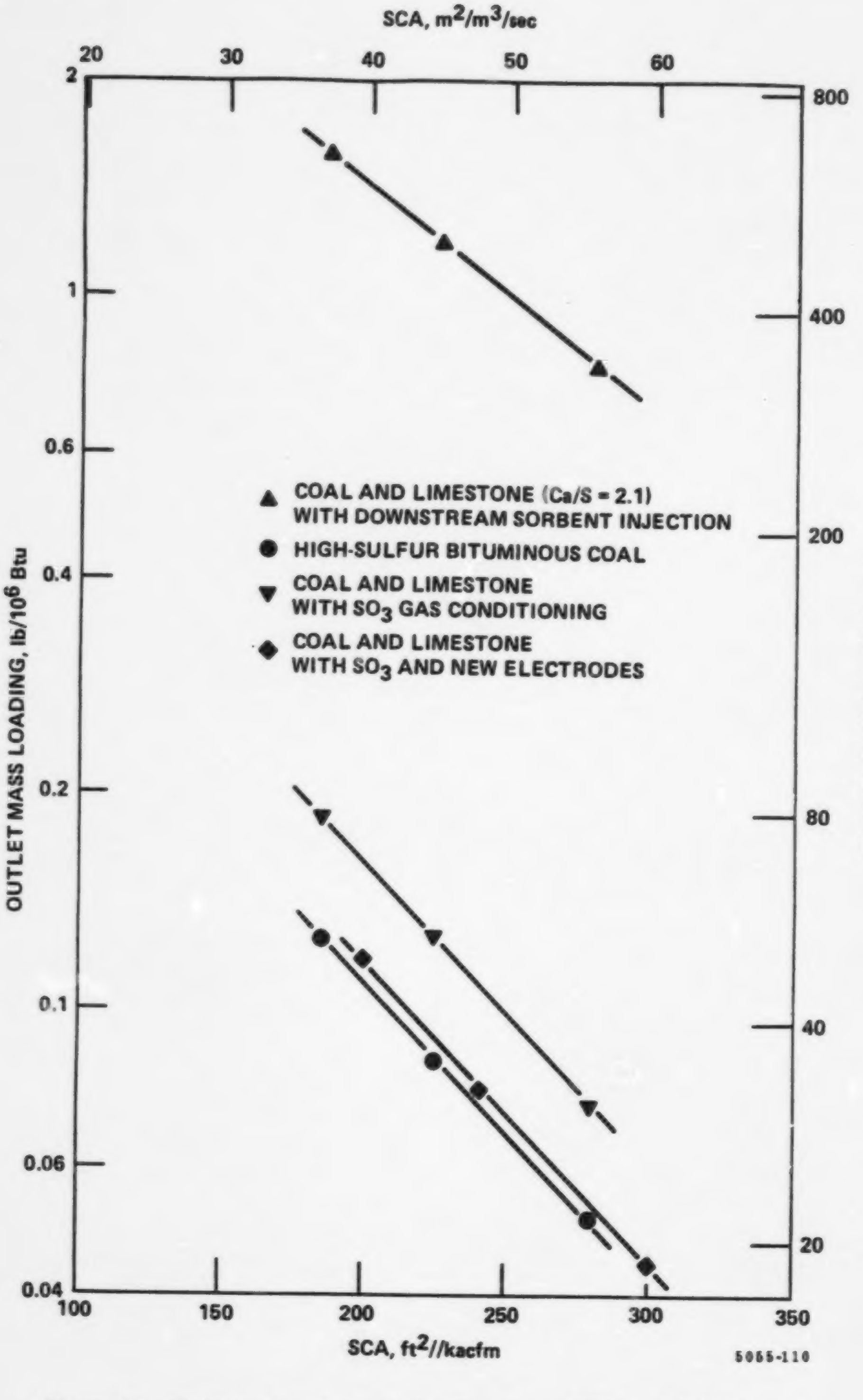


Figure 51. Calculated outlet mass loadings from ESP model simulation.

approximately 45% greater than the baseline case. However, the two-stage retrofit geometry further increases efficiency and results in predicted outlet mass loadings which closely approach the baseline case.

Results of further ESP simulations with hydrated lime as the sorbent have been reported by DuBard et al. (27). These simulations showed that some form of flue gas conditioning would be required to maintain good electrical operation of the ESP with hydrated lime injection. The flue gas conditioning may have to be accompanied by modification of the ESP electrodes and improvement of the gas flow distribution, depending on the size of the ESP.

SECTION 4

CONCLUSIONS AND RECOMMENDATIONS

IMPROVEMENTS IN SULFUR CAPTURE PERFORMANCE

The pilot-scale tests at SRI have shown that hydrated lime generally gives better SO_2 capture than ordinary limestones. The limestones generally do not perform well enough to meet the levels of SO_2 capture that are desired for the LIMB program (if the Ca/S ratio is limited to 2 or less). This is not to say, however, that a limestone could not be treated prior to injection to produce a satisfactory sorbent material.

This work has confirmed that BET surface area is an important factor in influencing the SO_2 capture, but there have been some indications that pore characteristics may also be important. Particle size also appears to be a potentially significant factor as indicated by the studies of sorbent utilization in various particle size fractions. The practical significance of this finding may be limited, however, due to the high cost of fine grinding.

In general, the best results have been obtained with hydrated lime, which is a fine (mmd ~2 μm) material, injected at a temperature in the range of 2000 to 2300°F. Burner injection of the hydrated lime is contraindicated.

ESP UPGRADES FOR SORBENT INJECTION

Furnace injection of calcium-containing sorbents produces high resistivity ash/sorbent mixtures in the absence of small residual concentrations of sulfur trioxide. With limestone as the sorbent, resistivity can be reduced to acceptable levels with SO_3 conditioning. If hydrated lime is the sorbent, the in situ response of resistivity to SO_3 is dependent upon the location of sorbent injection in the furnace. With both limestone and hydrated lime as sorbents, the laboratory resistivity of the resulting ash/sorbent mixture is reduced to less than 10^{10} ohm cm at equilibrium with 5 ppm SO_3 and 8% water vapor at 149°C (300°F). The resistivity of ash/sorbent mixtures produced with limestone injection is also reduced by increasing water vapor concentrations.

Burner injection of limestone produces large increases in submicron particle concentrations in the 0.1- to 0.6-μm diameter range compared with coal firing without sorbent injection. Downstream injection of limestone produced a cumulative mass loading at 10-μm diameter approximately 60% greater than the baseline case at a nominal calcium-to-sulfur ratio of 2 to 1. Injection of either limestone or hydrated lime near the furnace exit did not produce an increase in ultrafine (<0.6-μm) particle concentrations, as determined by an ultrafine sampling system.

Simulations of precipitator performance indicate that outlet emissions of less than 43 ng/J (0.1 lb/10^6 Btu) are achievable with sorbent injection at a specific collection area of 59 m^2/m^3/sec (300 ft^2/1000 ft^3/min) if conditioning restores electrical conditions to the values obtained prior to sorbent addition. Modifications of electrode geometry, when combined with a successful conditioning process, have the potential of significantly increasing performance over the values predicted for conventional ESP designs.

RECOMMENDATIONS FOR FUTURE WORK

Further Enhancement of Sorbent Performance

Additional laboratory and pilot-scale testing is needed to investigate the potential for improved sorbent utilization by the production of enhanced surface areas, optimized pore size characteristics, and reduced particle sizes. The use of modified calcination and hydration techniques should be explored as a means of influencing these key sorbent properties. Two potentially fruitful approaches are: (1) precalcination of limestone at relatively low temperatures and low CO_2 concentrations, (2) hydration of quicklime (CaO) in the presence of additives designed to enhance surface area and promote reactivity (28).

Recent work (29) has shown that the ash/sorbent mixtures produced in the LIMB process can be hydrated and recycled for additional SO_2 capture and improved sorbent utilization. This concept merits considerable attention in view of its potential to reduce sorbent consumption, improve sorbent utilization, reduce waste production, and reduce overall costs. An intriguing variation on this concept is the use of a coarsely ground limestone which produces calcine particles that will drop out of the flue gas ahead of the particulate collector or in the first field of an ESP. This allows the fly ash to be separated from the coarse calcine particles, which are then collected and conveyed to a hydrator. The hydrated material is injected back into the furnace, where it captures SO_2 with essentially the same effectiveness as commercial hydrated lime. Thus, the process produces the effectiveness of hydrated lime at the cost of coarse limestone. In view of this potential, considerable effort should be devoted to testing and evaluating this concept as well as the general concept of recycle.

Additional Impacts of Sorbent Injection on ESP Performance

Recent experience in Europe (30) has revealed problems with the formation of tenacious deposits on ESP electrodes when sorbent is injected into the backpass of utility boilers. This is a problem that has not been addressed in previous studies. The conditions under which these electrode deposits are formed need to be identified, and the ability of existing rapping systems to remove these deposits needs to be assessed. A small-scale sidestream ESP or a small portion of a full-scale ESP equipped for variable rapping intensity and accelerometer measurements should be employed at a site where the LIMB process is being used. Such testing may be a desirable addition to the LIMB Demonstration test program to be conducted at the Edgewater Plant of Ohio Edison in 1987. The handling and disposal of the LIMB ash are also issues that need to be addressed.

A complete evaluation of the SO_3 conditioning of LIMB ash requires the accurate measurement of residual gas-phase SO_3 levels. Accurate measurements are not possible with the Cheney-Homolya sampling system in its present configuration due to loss of SO_3 on the filter. A modified sampling procedure that is not susceptible to this problem is needed. Three possible approaches to modifying the sampling procedure are: (1) Removing the particulate in a cyclone or other collector at the front-end of the sampling probe so there is no filter cake through which the sample must be drawn, (2) injecting a gas at the mouth of the probe that will react with the CaO in the particulate rendering it ineffective for SO_3 pickup, or (3) injecting a gas that will react with the SO_3 forming an aerosol that can be collected on a filter and weighed. Even if the filter cake can be eliminated, there is still potential for loss of SO_3 in the cyclone or other particulate collector. Therefore, the latter two approaches are favored. In the case of item (2), the gas could be HCl that would react with the CaO forming $CaCl_2$ which should not capture SO_3. In the case of item (3), the gas could be NH_3 which would form an $(NH_4)_2SO_4$ fume.

The use of H_2O conditioning as a means of reducing LIMB ash resistivity should also be investigated. This form of conditioning also offers the advantages of reduced flue gas volume corresponding to the decrease in flue gas temperature. There is also some evidence that H_2O injection may "reactivate" the LIMB ash particulate producing additional downstream SO_2 capture. These effects should be demonstrated and quantified through laboratory and pilot-scale tests. If appropriate, this concept may also be incorporated into the plans for the LIMB Demonstration.

REFERENCES

1. Martin, G. B., and J. H. Abbott. Technical Status of EPA's LIMB Program. In: Proceedings: 1985 Symposium on Stationary Combustion NO_x Control, Volume 2, EPA-600/9-86-021b (NTIS PB86-225059), pp. 59-1 through 59-11, July 1986.

2. Kirchgessner, D. A. Laboratory-Scale Production and Characterization of High-Surface Area Sorbents. In: Proceedings: First Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, Volume 1, EPA-600/9-85-020a (NTIS PB85-232353), pp. 9-1 through 9-21, July 1985.

3. Borgwardt, R. H., and K. R. Bruce. EPA Study of Hydroxide Reactivity in a Differential Reactor. In: Proceedings: 1986 Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, Volume 1, EPA-600/9-86-029a (NTIS PB87-120465), pp. 15-1 through 15-18, October 1986.

4. Borgwardt, R. H., N. F. Roache, and K. R. Bruce. Surface Area of Calcium Oxide and Kinetics of Calcium Sulfide Formation. Environ. Prog., 3:129, 1984.

5. Case, P. L., M. P. Heap, R. Payne, and D. W. Pershing. LIMB Testing: The Use of Dry Sorbents to Reduce Sulfur Oxide Emissions from Pulverized Coal Flames Under Low-NO_x Conditions. In: Proceedings of the 1982 Joint Symposium on Stationary Combustion NO_x Control, Volume I, EPA-600/9-85-022a (NTIS PB85-235604), pp. 25-1 through 25-25, July 1985.

6. Ohmine, S., R. J. Martin, J. T. Kelley, and E. K. Chu. Low-NO_x Tangential System SO_x Control Through Sorbent Injection. Ibid. pp. 22-1 through 22-19.

7. Barrett, W. J., J. P. Gooch, R. S. Dahlin, R. M. Riggin, and H. D. Roth. Planning Studies for Measurement of Chemical Emissions in Stack Gases of Coal-Fired Power Plants. EPRI EA-2892, Electric Power Research Institute, Palo Alto, CA, March 1983.

8. Abbott, J. H., J. P. Gooch, and J. D. Kilgroe. Effects of Furnace Injection of Sorbent for SO_2 Control on Electrostatic Precipitator Technology and Requirements. Paper presented at International Conference on Electrostatic Precipitation, Kyoto, Japan. November 12-15, 1984.

9. Beittel, R., J. P. Gooch, E. B. Dismukes, and L. J. Muzio. Studies of Sorbent Calcination and SO_2-Sorbent Reactions in a Pilot-Scale Furnace. In: Proceedings: First Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, Volume 1, EPA-600/9-85-020a (NTIS PB85-232353), pp. 16-1 through 16-33, July 1985.

10. Steam/Its Generation and Use. 38th ed. Babcock & Wilcox Co., New York, NY. 1972.

11. Borgwardt, R. H., K. R. Bruce, and J. Blake. EPA Experimental Studies of the Mechanisms of Sulfur Capture by Limestone. In: Proceedings: First Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, Volume 1, EPA-600/9-85-020a (NTIS PB85-232353), pp. 6-1 through 6-20, July 1985.

12. Slaughter, D. M., S. L. Chen, and W. R. Seeker. Enhanced Sulfur Capture by Promoted Calcium-Based Sorbents. In: Proceedings: 1986 Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, Volume 1, EPA-600/9-86-029a (NTIS PB87-120465), pp. 12-1 through 12-24, October 1986.

13. Nichols, G. B. Techniques for Measuring Fly Ash Resistivity. EPA-650/2-74-079 (NTIS PB 244140), U.S. Environmental Protection Agency, Research Triangle Park, NC, August 1974.

14. Bickelhaupt, R. E. Measurement of Fly Ash Resistivity Using Simulated Flue Gas Environments. EPA-600/7-78-035 (NTIS PB 278758), U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1978.

15. Harris, D. B. Procedures for Cascade Impactor Calibration and Operation in Process Streams. EPA-600/2-77-004 (NTIS PB 263623), U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1977.

16. Johnson, J. W., G. I. Clinard, L. G. Felix, and J. D. McCain. A Computer-Based Cascade Impactor Data Reduction System. EPA-600/7-78-042 (NTIS PB 285433), U.S. Environmental Protection Agency, Research Triangle Park, NC, March 1978.

17. Johnson, J. W., B. E. Pyle, and W. B. Smith. Extending Precision in a Computer-Based Cascade Impactor Data Reduction System. In: Proceedings: Advances in Particle Sampling and Measurement. EPA-600/9-80-004 (NTIS PB80-187487), U.S. Environmental Protection Agency, Research Triangle Park, NC, January 1980. pp. 146-166.

18. Liu, B. Y. H., and D. Y. H. Pui. On the Performance of the Electrical Aerosol Size Analyzer. J. Aerosol Sci., 6:149-164, 1975.

19. Liu, B. Y. H., R. N. Berglund, and J. K. Agarwal. Experimental Studies of Optical Particle Counters. Atmos. Environ., 8:717-732, 1974.

20. Felix, L. G., R. L. Merritt, J. D. McCain, and J. W. Ragland. Sampling and Dilution System Design for Measurement of Submicron Particle Size and Concentration in Stack Emission Aerosols. TSI Quarterly, 7, October-December 1981.

21. Cheney, J. L., and J. B. Homolya. Sampling Parameters for Sulfate Measurement and Characterization. Environ. Sci. Technol., 13:584-588, 1979.

22. Gooch, J. P., R. E. Bickelhaupt, G. H. Marchant, R. D. McRanie, L. E. Sparks, and R. F. Altman. Improvement of Hot-Side Precipitator Performance with Sodium Conditioning—An Interim Report. J. Air Pollut. Control Assoc., 31:291-297, 1981.

23. Bickelhaupt, R. E., and L. E. Sparks. An Improved Model for Predicting Fly Ash Resistivity. In: Proceedings: Sixth Symposium on the Transfer and Utilization of Particulate Control Technology, Volume 1, EPA-600/9-86-031a (NTIS PB87-147617), pp. 11-1 through 11-17, December 1986.

24. Dahlin, R. S., and R. F. Altman. Prediction of Mass Loading and Particle Size Distribution for Use in a Precipitator Sizing Procedure. Paper presented at the EPRI Conference on Electrostatic Precipitator Technology for Coal-Fired Power Plants, Nashville, TN. July 14-16, 1982.

25. Faulkner, M. G., and J. L. DuBard. A Mathematical Model of Electrostatic Precipitation (Revision 3): Vols. I and II. EPA-600/7-84-069a and -069b (NTIS PB84-212679 and -212687), U.S. Environmental Protection Agency, Research Triangle Park, NC, June 1984.

26. Durham, M. D., G. A. Rinard, D. E. Rugg, and T. Carney. "Pilot-Plant Evaluation of the Cooled Electrode Precharger on a Utility Flue Gas Slipstream with High Resistivity Fly Ash. In: Proceedings: 77th Annual Meeting of the Air Pollut. Contr. Assoc., San Francisco, CA. June 24-29, 1984.

27. DuBard, J. L., J. P. Gooch, R. Beittel, S. L. Rakes, and G. R. Offen. Particle Properties Related to ESP Performance with Sorbent Injection and Gas Conditioning. In: Proceedings: 1986 Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, Volume 2, EPA-600/9-86-029b (NTIS PB87-120457), pp. 36-1 through 36-18, October 1986.

28. Gooch, J. P., E. B. Dismukes, R. Beittel, J. L.Thompson, and S. L. Rakes. Sorbent Development and Production Studies. In: Proceedings: 1986 Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, Volume 1, EPA-600/9-86-029a (NTIS PB87-120465), pp. 11-1 through 11-29, October 1986.

29. Dahlin, R. S., C. L. Lishawa, and N. Kaplan. Analysis of LIMB Waste Management Options. In: Proceedings: 1986 Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, Volume 2, EPA-600/9-86-029b (NTIS PB87-120457), pp. 39-1 through 39-24, October 1986.

30. Chughtai, M. Y. Results of Direct Desulfurization from Commercial Power Plants. Ibid. pp. 43-1 through 43-9, October 1986.

APPENDIX A. QUALITY ASSURANCE PROCEDURES

This section describes quality assurance procedures used in tests performed in this research project. Other sections of this report, as well as the Quality Assurance Project Plan submitted in March 1983, contain detailed descriptions of individual instruments, procedures, and QA goals used throughout this program. The following are descriptions of QA procedures executed in project work, with numerical examples of the results. Detailed records are available in laboratory notebooks and forms, but are not included in this report.

Continuous Gas Analysis

Instrument calibration. The continuous gas analyzers used in the project were:

- Beckman Model 755 Paramagnetic, O_2
- Beckman Model 864 Nondispersive Infrared, CO_2
- DuPont Model 400 Ultraviolet, SO_2
- ThermoElectron Model 10 Chemiluminescent, NOx
- Horiba Model PIR-2000 NDIR, CO

All instruments were calibrated daily (or more often, at the discretion of the operator) using compressed gases. The calibration gases used throughout this program are listed in Table A1. The general procedure was to adjust the calibration gas flow rate to the same value used for the sample gas using common rotameters downstream of the switching valves, and then adjust the instrument to read zero and span values as required. Zero and span gases were alternated until no further adjustments were required. The time of calibration and any problems (e.g., unusually large deviation from the expected values) were noted on the recorder charts and in the project notebook.

Since the sulfur dioxide content of the flue gas was a major focus in this work, additional quality assurance procedures were implemented for the DuPont Model 400 analyzer. These included multipoint calibrations, use of NBS Standard Reference Materials (SRMs), and the keeping of detailed records of instrument calibration and performance. Moreover, validation of the entire sample extraction, conditioning, and analysis system for determination of SO_2 concentration was performed as described subsequently.

Daily calibration of the SO_2 analyzer was performed using a single, Matheson Primary Standard grade gas. A log of instrument response and dial settings before and after calibration was kept using the Daily Calibration Record. (Copies of this form and the instruction sheets for its use are included at the end of this section.)

Precision and accuracy of the SO_2 analyzer may be estimated from a record of the instrument response to span gas taken during the daily calibration before adjustment to the span value. Forty-one such values recorded over a six-month period yielded the following:

Span gas concentration	1997 ppm
Average of 41 values	2011 ppm

TABLE A1. CALIBRATION GASES

Type	Grade[1]	Cylinder No.	Period Of Use	Concentration
Zero, all	extra dry	NA	NA	99.9%
	prepurified	NA	NA	99.998%
CO span	certified	SX14216	2/83 - 6/85	304 ppm
O_2/CO_2 span	primary	LK202546	82 - 83	5.00%/15.0%
	certified	SX15874	2/84 - 6/85	5.04%/14.91%
NO span	EPA protocol	SX13746	3/83 - 2/84	493 ppm
NO span	certified	31266T	2/82 - 3/83	~900 ppm
NO span	certified	SX11927	2/84 - 3/85	888 ppm
NO span	certified	SX16833	3/85 - 6/85	1020 ppm
SO_2 span	primary	10117T	8/82 - 3/83	1500 ppm
SO_2 span	EPA protocol	SX12155	3/83 - 2/84	543 ppm
	EPA protocol	SX11960	3/83 - 2/84	2461 ppm
SO_2 span	primary	SX16247	2/84 - 6/85	1003 ppm
	primary	SX12137	2/84 - 6/85	1997 ppm
	primary	SX14188	2/84 - 6/85	2988 ppm
	primary	31821	3/85 - 6/85	1997 ppm
SO_2 span	NBS SRM 1662a	FF-19957	3/85 - 6/85	945 ppm
	NBS SRM 1663a	FF-19652	3/85 - 6/85	1439 ppm
	NBS SRM 1664a	FF-16938	3/85 - 6/85	2440 ppm

1. Most gases supplied by Matheson Gas Products; tolerance on certified grades ±2% of component, tolerance on primary grade ±1% of component.

SRM supplied by NBS; tolerance 1% of component.

Standard deviation, ppm	120
Standard deviation, %	6.0
Average of $\frac{\lvert Xi-1997 \rvert x100}{1997}$	3.6

The values 6.0 and 3.6% represent the precision and accuracy, and are well within the respective goals of 10 and 5% for this measurement. Note that the record used to arrive at the foregoing accuracy and precision included readings taken after 2-day to 2-week down periods, whereas calibration always preceded actual tests by less than 24 hours.

Multipoint calibrations were performed periodically to determine instrument linearity and to verify the concentration of the single calibration gas used for daily adjustments. Figure A1 shows an example of this technique. The instrument was first calibrated using the Daily Calibration procedure with 1997 ppm Matheson Primary Standard gas. Then, without further adjustment to the instrument, three NBS Standard Reference Materials were sampled. Linearity was excellent, and the absolute values of the SRM materials were within the tolerances given by NBS.

Gas sampling and conditioning. The sample was withdrawn through an in-stack, porous, stainless steel filter. The in-stack filter was about 18-in long and 3/4-in in diameter, and was located on the centerline of the 4-in diameter stack. The flue gas velocity at this point was typically 40-80 ft/s, while at the nominal sample flow of 15 scfh the filter face velocity was about 0.02 ft/s. This geometry resulted in little buildup of solids on the probe.

The sample was conveyed through a heated Teflon line to a conditioner where water vapor was removed by condensation in Teflon coils immersed in 32 - 40°F coolant. A second in-line filter upstream of the conditioner ensured that all particulate was removed from the gas before cooling. Multiple samples (reference: C442-24) taken from the conditioner showed that the conditioned gas water content was 0.5 to 1 vol%; analyses using this system are reported as "dry basis" without further correction.

The gas sample was distributed through switching valves to individual analyzers. Analyzer calibration gases were supplied through these switching valves as well. Analyzer calibration was discussed above; potential problems not addressed by analyzer calibration include loss of a constituent gas to solids on either the in-stack or in-line filter, and loss of sample to the condensate within the conditioner. Equilibrium calculations showed that the potential loss of SO_2 to the water of combustion (in the absence of alkaline solids)was about 1.5% for coal, or 3% for natural gas. This loss was deemed acceptable, particularly since the variable of interest was the change in SO_2 concentration with sorbent addition.

In order to verify that penetration of solids into the conditioner (which would invalidate the equilibrium calculation) was insignificant, the condensate was collected during coal combustion and intermittent addition of either dolomitic or calcitic hydrated lime (Reference: C442-82,154). The total sulfur

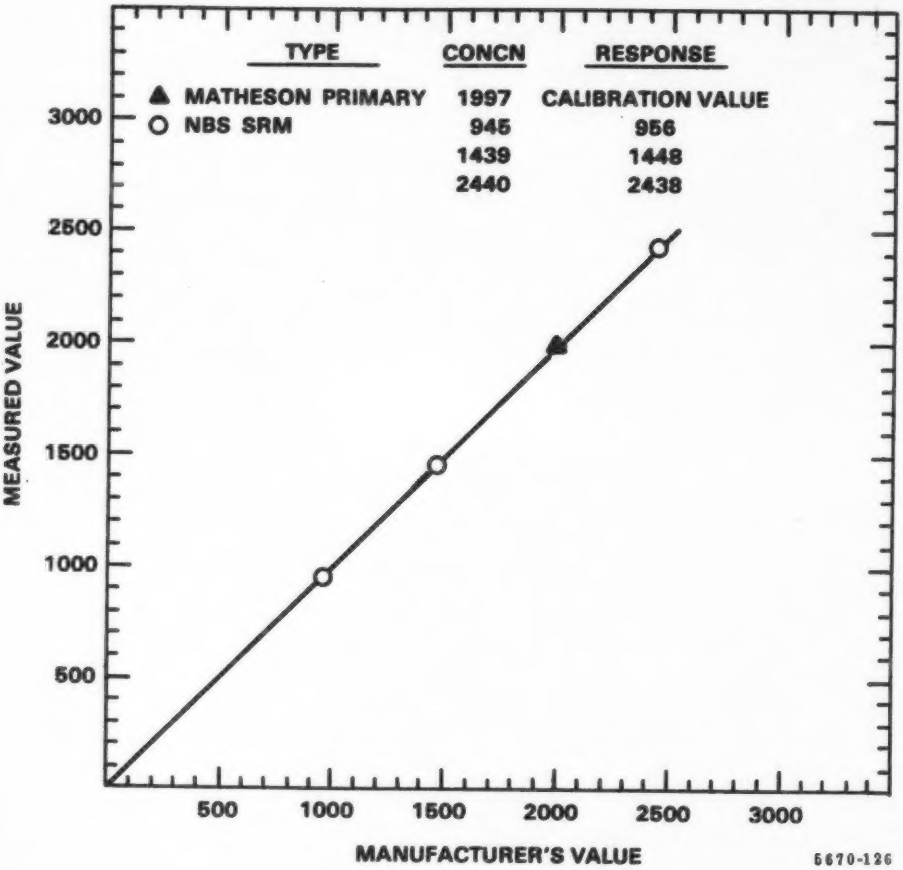


Figure A1. Multipoint calibration of Dupont SO_2 Analyzer.

content of the condensate corresponded to 0.6 to 1% of the SO_2 in the gas sample. The calcium in the condensate was equivalent to less than 0.02 ppm in the gas. These samples indicated that the sorbent was effectively removed by the filters, and that the condensate did not remove a significant portion of the gas-phase SO_2.

Two additional tests were performed periodically to verify that the sample system was not contributing to measured SO_2 removal. In these tests, a known amount of SO_2 was injected upstream of the sample probe. The measured value of SO_2 was compared to that calculated from the injection rate and fuel rate.

In the first type of test, SO_2 was added at a point near the sample probe during gas firing and furnace sorbent injection. This test is especially severe in that the probe is exposed to unsulfated calcine (conveyed from the furnace during the period when no SO_2 is added except at the probe). Near-probe removal of SO_2 was 1.5 to 2.4% for furnace injection of limestone or calcitic lime at Ca/S = 2, and about 4% with furnace injection of dolomitic lime. This test does not distinguish between removal in the combustor near the probe and removal on the probe or in the conditioner. Still, these results were considered satisfactory.

In the second, more realistic type of test, SO_2 was injected near the sampler during coal combustion and furnace sorbent injection. In this case, the recovery of an incremental SO_2 concentration in the presence of sulfated sorbent is measured. The recovery of the injected SO_2 ranged from 100 to 103% of the calculated value with furnace injection of either calcitic or dolomitic lime, and was 102% in the absence of sorbent injection. Recovery greater than 100% may result from errors in the coal composition used to calculate concentration; the important point is that recovery did not change with sorbent addition.

Readouts. Voltage outputs from all analyzers were recorded on 24-hr chart recorders in order to have a complete record of furnace operation. These recorders were periodically calibrated according to the manufacturers' instructions using a Ronan voltage source. These chart recorder traces were used only as backup and to assure a complete record.

A Soltec 2-pen recorder was used to record the SO_2 analyzer output and the analog output from the gravimetric sorbent feeder during all sorbent addition tests. This recorder provided a copy which could be entered in the laboratory notebook along with the numerical data for each test, in order to provide a visual record of the response time and stability of the test. Again, chart recorder output was not used to determine the numerical results.

A Cyborg Isaac 41A data aquisition system using an Apple IIe computer was used to log all gas compositions and perform preliminary calculations. The standard delta-SO_2 program, for example, logged O_2, SO_2, and CO_2, as well as SO_2 and CO_2 corrected to a constant oxygen (3%) value, at one-minute intervals; average baseline and controlled values of SO_2 were then calculated over fixed time intervals. Other programs were written for instrument calibration, temperature logging (fixed thermocouple), etc.

The Isaac system calibration was limited to adjustment of a zero-offset potentiometer. The linearity and software conversions were checked with the following comparison to a Keithley digital volt meter (DVM) (reference C442-79):

Analyzer	O_2	CO_2	SO_2
range	0-10%	0-20%	0-4000 ppm
full scale output	1.0 v	10 mv	10 mv
zero response			
DVM, voltage	0.00 v	0.0 mv	0.0 mv
DVM, equiv.	0.00%	0.0 ppm	0.0 ppm
Isaac output	0.08%	0.1%	20 ppm
span response			
DVM, voltage	0.500 v	7.50 mv	6.05 mv
DVM, equiv.	5.00%	15.0%	2420 ppm
Isaac output	4.97%	15.0%	2425 ppm

Fuel, sorbent, and additive rates

Coal rate. Coal was fed with an Acrison gravimetric feeder. At the start of each test period the coal feed rate was determined by weighing the discharge collected from the feeder, at the rate to be used in the test. Typical results were:

date	time	set point, lb/hr	net lbs	time, min	lbs/hr
3/27/84	0100	75	12.50	10.0	75.0
3/27/84	0130	75	12.40	10.0	74.4
4/3/84	0220	75	12.50	10.0	75.0
4/3/84	0240	75	12.46	10.0	74.6

Provisions exist for calibrating the feeder should the actual feed rate not match the set point. As shown by the above tests, this was not normally necessary with the coal feeder, since it typically fed within 1% of the set point.

Sorbent rate. Sorbent was fed either with an Acrison volumetric feeder or with an Acrison gravimetric feeder. In general, gravimetric sorbent feeding was less reliable than with coal, due to the smaller feed rates (typically 5-20 lb/hr) and the material properties. Feed rate tests were performed at least once for each new rate, or more often as required to achieve a close match to the desired feed rate (i.e., Ca/S). In addition, the policy adopted for a "standard" delta-SO_2 test was to perform a feed rate test immediately before and after each delta test with no intervening adjustments to the feeder. As an example of this procedure consider the following tests in which hydrated lime was the sorbent:

Test No.	Feed Rate Tests, lbs/hr			range
C-751-xx	pre	post	average	+/-%
98	8.20	8.17	8.19	0.3
99	8.17	7.84	8.01	2.0
100	7.84	7.10	7.47	5.0
102	7.60	6.40	7.00	9.4
103	6.40	6.44	6.42	0.3
104	6.44	6.01	6.22	3.4

Accuracy relative to the target feedrate is not really an issue, since test results are based on the actual Ca/S for each test. The foregoing procedure should place an upper limit on the uncertainty for each rate test. Since the feedrate tends to decline as a test proceeds (until the feeder is refilled or the speed is changed), the "pre" and "post" rates should bracket the actual rate fed during the test rather than being randomly distributed about some target mean.

Natural gas. The feedrate of natural gas was set using a Waukee rotameter. The rotameter reads directly in SCFH for a gas specific gravity of 0.6 (relative to air), a line pressure 16.7 psia, and a temperature of 70°F. The correction factor provided by the manufacturer was

$$\text{SCFH} = (\text{CFH as-read})*((\text{psia}/16.7)*(530/{}^{\circ}\text{R})*(\text{SG}/0.6))^{0.5}$$

This equation was used to correct the gas rate for calculation of molar flue gas flow. The composition of the natural gas was provided by the local utility; the gas specific gravity was 0.58. The rate determined with the rotameter was checked periodically by isolating the furnace gas supply and reading the utility dry gas meter located upstream. The dry gas meter has an internal correction for average local barometric pressure and line pressure; correcting for temperature only gave the following results for simultaneous readings (reference C409-52):

Rotameter				Dry gas meter			Rotameter-to-Dry gas meter Flow Ratio,
CFH	psig	°F	SCFH	CFH	°F	SCFH	SCFH/SCFH
735	2.19	55	759	716	45	752	1.009
1000	2.00	57	1025	981	45	1029	0.996

Sulfur dioxide. Sulfur dioxide was added to the system either at the burner during gas-fired sorbent tests, or downstream for sample system validation tests. The anhydrous-grade (99.98% minimum analysis) gas was supplied from

150 lb (net) cylinders. The rate was controlled using a Matheson No. 604 rotameter tube. The manufacturer's calibration for sulfur dioxide was used with the following correction factor:

$$\text{s} \quad \text{flow} = \text{flow as-rd} *((P/Pcal)*(Tcal/T))^{0.5}$$

Most tests were too short in duration to determine cylinder weight loss accurately, and were therefore controlled only with the rotameter. However, the rotameter calibration and correction factors were validated with weight loss measurements on several occasions with long-term SO_2 addition. Rotameter readings compared to weight loss over a 16 hour period as follows (reference: C-442-5:24):

cylinder wt.	2235 hrs, 2/7/84	202.00 lbs
	1508 hrs, 2/8/84	112.88 lbs

89.12 lb/16.55 hrs =5.38 lbs/hr

	1430 hrs 2/7/84	1508 hrs 2/8/84
Rotameter pressure	16 psig	16 psig
Temperature	81°F	70°F
Barometric pressure	29.83 in Hg	29.86 in Hg
Flow rate as-read	10.5 l/m	10.5 l/m
Corrected flow rate	5.32 lb/hr	5.26 lb/hr
Rotameter flow/wt loss	0.989	0.978

This test indicated that manual control using the general calibration and correction factors gave a flow rate accurate within about 2% of the true rate.

Weight loss. The preceding calibrations using weight loss or discharge weight used one of these two balances:

Test	Typical Weights (net)	Balance	Minor Division	Calibration Weights
Sorbent feed rate	100-500 g	Ohaus Dial-O-Gram	0.1 g	1 lb
Coal feed rate	10-20 lb	Howe Model 5400	1 oz (0.063 lb)	1,10, 25 lb
SO_2 feed rate	5-100 lb	Howe Model 5400	1 oz (0.063 lb)	1,10, 25 lb

The balances read within one minor division of the calibration values shown after zero adjustment. The calibration weights were certified Class F weights having a tolerance of 0.015% (1 lb wt) to 0.01% (10 and 25 lb weights). In all cases, the calibration tolerance and minor scale divisions were adequate to guarentee accuracy to 1% or better for the application listed.

Gross and net weights were of the same order for coal and sorbent tests. Sulfur dioxide rates were typically 5 lbs/hr, with an initial gross cylinder weight of 200 lbs. Calibration for this test was therefore checked by noting the increment in scale reading when a calibration weight was placed on the scale with the full cylinder. Again, the balance read correctly to within a minor division.

Mineral Analysis

The analytical procedures used in the analysis of fly ash, sorbent, and fly ash/sorbent samples were evaluated with different portions of NBS, SRM 1c Limestone and SRM 1633a Fly Ash. These results are shown in the following tables:

SRM 1633a FLY ASH

Parameter	wt%			
	Sample 1	Sample 2	Average	True Value
Lithium	0.02	0.02	0.02	a
Sodium	0.18	0.18	0.18	0.17
Potassium	1.9	1.8	1.85	1.88
Magnesium	0.45	0.47	0.46	0.455
Calcium	1.1	1.3	1.2	1.11
Iron	9.7	9.5	9.6	9.4
Titanium	0.84	0.78	0.81	(0.8)[b]
Phosphorus	0.24	0.21	0.225	a
Aluminum	14.2	14.2	14.2	(14)[b]
Silicon	22.7	22.8	22.75	22.8
Sulfur	0.10	0.18	0.14	a

a Not determined by NBS

b Values in parentheses are not certified values.

SRM 1c LIMESTONE

Parameter	wt%			
	Sample 1	Sample 2	Average	True Value
Lithium oxide	0.01	0.01	0.01	a
Sodium oxide	0.03	0.02	0.025	0.02
Potassium oxide	0.27	0.30	0.285	0.28
Magnesium oxide	0.42	0.42	0.42	0.42
Calcium oxide	50.4	50.8	50.6	50.3
Iron oxide	0.58	0.58	0.58	0.55
Titanium dioxide	<0.2	<0.2	<0.2	0.07
Phosphorus pentoxide	0.14	0.07	0.105	0.04
Aluminum oxide	1.4	1.3	1.35	1.3
Silicon dioxide	7.0	6.7	6.85	6.84
Sulfur trioxide	0.18	0.14	0.16	a

a Not determined by NBS

Seven different batches of an Eastern U.S. fly ash were analyzed to determine the precision of the analytical procedures. The following results were obtained:

Parameter	Average wt%	% RSD
Lithium oxide	0.07	0
Sodium oxide	0.30	1.2
Potassium oxide	2.6	0
Magnesium oxide	0.88	1.6
Calcium oxide	2.1	2.5
Iron oxide	11.0	0.82
Titanium dioxide	1.9	3.0
Phosphorous pentoxide	0.69	1.1
Aluminum oxide	29.1	0.94
Silicon dioxide	49.2	0.57
Sulfur trioxide	0.55	12.0

Surface Area Measurements

Single-point Brunauer, Emmett, and Teller (BET) surface area determinations were made with a Quantachrome Monosorb analyzer. Two Quantachrome reference materials were used to verify the calibration of the instrument during the course of this contract. The results of these measurements, as well as measurements of the surface area of various sorbents, are shown below:

Sample	True value m^2/g	Found m^2/g	Average m^2/g
Quantachrome No. 2008	5.15	4.92, 4.94, 4.83, 4.91, 4.90	4.90
Quantachrome No. 2005	113	115, 110, 115	113
Calcined Genstar sorbent	--	40.6, 41.0, 40.6, 40.6	40.7
Reagent grade $Ca(OH)_2$	--	11.4, 11.4, 11.9	11.6
Longview hydrate	--	21.1, 21.2, 21.1, 21.5	21.2

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DAILY CALIBRATION RECORD
DuPont Model 400 SO_2 Analyzer

Line	Value	Comments
1. Date		
2. Time start		
3. Operator		
4. Flow rate, CFH		
5. Cell temp, °F		
6. P_B, in Hg		
7. Zero gas		
8. Span gas/bottle No.		
Before Calibration		
9. Range		
10. Zero dial		
11. Span dial		
12. Response to zero		
13. Optical		
14. Span		
15. Span + optical		
After Calibration		
16. Range		
17. Zero dial		
18. Span dial		
19. Response to zero		
20. Optical		
21. Span		
22. Span + optical		
23. Time complete		

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Instructions for Completing Daily SO_2 Analyzer Calibration

1. Date. Enter date as MM/DD/YY.

2. Time. Enter time as hhmm, in 24-hr format.

3. Operator. Enter initials.

4. Flow rate, CFH. Read sample flow rate passing through DuPont analyzer from rotameter on panel, before any adjustments. (The flow should be adjusted whenever required to the prescribed rate. Nothing else should be changed without going through the entire procedure.)

5. Cell temp, °F. Enter temperature of sample cell, read from channel B9, fluke digital readout.

6. P_B, in Hg. Enter pressure read from control room barometer.

7. Zero gas. Enter type; for example, "N_2", "air".

8. Span gas/bottle. Example: "1997/31821" would give the manufacturer's concentration for cylinder 31821. In certain cases, a better value (determined by comparison with NBS standard reference material) clearly marked on the bottle would be entered.

9. Range. Enter range from DuPont front panel. Note that any range other than 0-4000 will require a change in Isaac software or use of a voltmeter and conversion factor to read ppm.

10. Zero dial. Enter reading from 0 to 1000 (read each full turn as a change of 100).

11. Span dial. Enter reading from 0 to 1000.

12. Response to zero. Switch selector valve to zero gas and allow readings to stabilize. Enter average reading.

13. Optical. With zero gas still flowing, raise optical filter into beam path (pull knob located in sample cell housing). This will stabilize very quickly. Record and return knob to down position.

14. Span. Switch selector valve to span gas and adjust flow. Allow to stabilize and enter response.

15. Span + optical. With span gas still flowing, raise optical filter, record, and return filter to lowered position. OMIT this step if span gas being used is >1400 ppm.

Calibration

a) After Step 15, adjust span dial so that instrument gives value from line 8 (±1%), with span gas flowing.

b) Return to zero gas, adjust flow, and allow to stabilize. Adjust zero dial to read 0 ± 10 ppm.

c) Repeat (a) and (b) only if adjustments in either step were major (>20 ppm); otherwise, fill in remaining lines.

Record lines 16-22 without any further adjustment (except for flow rate as required). See 9-15.

21. Span should be within 2% of line 8.

23. Time complete. Enter time. Switch back to sample and adjust flow. Mark 24-hr charts "zero + span, -- hrs".

Form CCF 012
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MULTIPOINT LINEARITY TEST
DuPont Model 400 SO_2 Analyzer

1. Date______________________
2. Start time________________
3. Operator__________________
4. Cell temp, °F_____________
5. Barometric pressure, in Hg__________
6. Flow rate, SCFH_____________________
7. Readout_____________________________
8. Range_______________________________

	Zero	Span 1	Span 2	Span 3	Span 4	Span 5	Optical
9. Type							
10. Bottle No.							
11. Manufacturer's value							
12. Other value							
13. Calibration value (enter one only)							
14. Zero dial________							
15. Span dial							
16. Analyzer response (no further adjustments)							
17. Stop time							

18. Comments____

* Page 2 of this form is a blank from which Figure A1 was taken. It is used in draft form so that the operator can plot the results for inspection.

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Instructions for Completing SO_2 Analyzer Multipoint Linearity Test

1. Date. Enter date as MM/DD/YY.

2. Start time. Enter time, hhmm, 24-hr format.

3. Operator. Enter initials.

4. Cell temp, °F. Enter temperature of sample cell unit, currently read from B9.

5. Barometric pressure. Read from barometer in control room.

6. Flow rate, SCFH. Read from rotometer on panel. Adjust to prescribed value for each gas.

7. Readout. Enter readout device to be used. In general, the Isaac data acquisition system is preferred.

8. Range. Enter range in ppm from front panel. Note that if range is other than 0-4000 ppm, the Isaac software must be changed, or a voltmeter and conversion factors must be used.

9. Type. Enter type or grade of gas; for example, "NBS SRM", "Matheson primary std.", "Union Carbide extra dry N_2".

10. Bottle No. Enter cylinder number given on tag of cylinder.

11. Manufacturer's value. Enter value on tag or bottle. Use certified rather than nominal or requested value.

12. Other value. Enter if a better value has been determined and affixed to cylinder ("better values" for non NBS cylinders may be determined by comparison with NBS SRM or by chemical analysis).

13. Calibration value. Enter one value only.

    Calibration. Instrument should zeroed and spanned (to one value) as in procedure from Daily SO_2 Analyzer Calibration. Repeat zero and span until values do not change.

14. Zero dial. Enter reading from 0 to 1000 (read each full turn as a change of 100).

15. Span dial. Enter reading from 0 to 1000.

16. Analyzer response. Determine response to various span gases without further adjustment of the instrument (flow rate should be adjusted for each new gas). One or more gases should be repeated.

17. Stop time. Enter time completed.

18. Comments. Describe any unusual factors. Results should be plotted and described. Least squares fit should be run.

19. Witness. Enter initials.